Wood Drying Condensate Treatment Using a Bio – Trickling Filter with Bark Chips as a Support Medium

A thesis submitted in partial fulfilment of the requirement for the degree of Master of Engineering in Chemical and Process Engineering

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Abstract

The kiln drying of wood produces huge amounts of vapour. The vapour is released to the environment when the process purges some of the saturated hot air. The main environmental issue regarding the use of kiln drying process are the release of the water vapour which contains organic contaminants. Some of them are hazardous to human health. In addition, there are some wood particles which may released with the water vapour purging process.

In this research, the vapour is condensed and analysed for its organic contaminants and their biodegradability. The result showed that the dominant contaminants present in the condensate were ethanol and methanol with the concentration of approximately 65 mg/L and 25 mg/L respectively. The average COD concentration of the condensate was 159 $\pm$ 40 mg/L. The analysis also showed that the contaminants were biodegradable.

In order to treat the wastewater, a trickling filter process using bark chips as a support medium was used to treat an artificial wastewater. The artificial wastewater contained the dominant contaminant present in the wood drying condensate. In the experiment, different sizes of bark chips were used. In addition, the loading rate of the treatment system was varied by changing the flow rate and contaminant concentration.

The 30 cm long trickling filter using bark chips varying between of 2.8 – 4 mm diameter as the support medium gave a maximum removal of 36.4 % with removal capacity of 8.34 kg COD/m^3_{bed}•day at a flow rate of 2.8 cm/min and average inlet COD load of 20.4 kg COD/m^3_{bed}•day. The trickling filter with bark chips varying between 5.6 – 8 mm diameter as the support medium was operated using variations in contaminant concentration and flow rate. The operation using different inlet concentration gave the highest removal rate of 13.5 kg COD/m^3_{bed}•day at average initial load of 84.9 kg COD/m^3_{bed}•day, flow rate of 2.8

cm/min and theoretical initial concentration of 680 mg/L. The trickling filter operated with flow rate variation showed the highest removal rate of 10 kg COD/m^3_{bed}•day at an average inlet load of 53.3 kg COD/m^3_{bed}•day and flow rate of 7.1 cm/min.

The removal rate of the contaminants in treatment was limited. There is a number of possible explanations. First is the active surface area, which indicating the area where the contact between the biofilm surface and feed happened. The active surface area increased as the flow rate increased. Second is the residence time of the feed in the bed. The residence time of the feed varied with the flow rate. It decreased as the flow rate increased. Third is the influence of the contaminants in the feed. The presence of methanol and methanol in the feed inhibited each other's degradation.

The dimention of a full-scale biotrickling filter to be used in actual kiln was also estimated. The estimation was made based on the maximum removal rate and optimum flow rate obtained in the experiments. The result of the estimation showed to obtain significant removal, the required bed would have to be 2.35 m in diameter and 160 in height.

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Chapter 1 Introduction

Waste treatment is an important aspect of an industry. Before people paid attention to environmental quality, most of the unused waste that came from industry went directly to the environment. Today, due to the increasing concerns about the present condition of the environment, laws and regulations are being introduced in order to preserve, or even repair the damage that has been done.

This change also applies to the wood processing industry in general and the wood drying industry in particular. Kiln drying of wood emits hydrocarbon compounds, which are released while the wood is dried. This emission has been neglected since there is no regulation limiting this emission. Due to the increased concerns for workplace safety, as well as the environmental requirements of the export markets, it is anticipated that the laws regarding those will be stricter in the future.

A proposed solution for kiln emission is to condense the water vapour in the gas that is purged periodically during the drying process. This treatment has two advantages. First, during the condensation process, most of the hydrocarbons are condensed as well, therefore reducing the emission level of the purged air. Second, the treated air is channelled back into the chamber, therefore reducing the heating cost since the recycled air is higher in temperature compared to the fresh air.

The condensation process transfers the hydrocarbon emission from the gas phase to the liquid phase. The next question is what type of treatment is suitable for treating the condensed water. There are several wastewater treatment technologies that can be used to remove the unwanted materials in the condensed water, such as activated sludge and bio-trickling filter. The choice depends on the quality and the quantity of the wastewater that needs to be treated.

1.1 New Zealand Wood Drying Industry

Kiln drying is one of many processes employed to produce dry wood from green timber for furniture and building material. It most commonly used nowadays because of its known efficiency and advantages compared to air drying. Preservation of wood also needs the wood to be dried to a certain moisture content for effective treatment to prevent chemical degradation, mechanical wear, and also from fungal and insect attack (Kininmonth et al. 1991). It also provides the wood with extra defence against fire and weather change (Walker 2006).

In the kiln drying of timber, hot air is used as the drying medium to remove the water present in the wood as water vapour. First, the air is heated by a heating element and blown to the wood chamber. The air will transfer its heat into the wood and to the water on the surface and inside it. The water from the surface will evaporate eventually and result in low moisture surface. The moisture gradient between the surface and the core will drive water to move from inside the wood to its surface.

During the drying process, the air will become humid with the water evaporated from the wood. In order to maintain the required humidity and the driving force for the evaporation of water from the wood, some of the humid air will be released and fresh air will be introduced into the process. The process is done automatically and depends on the setting of the wet bulb and dry bulb in the chamber.

1.2 Issues

Kiln drying process emits volatile organic compounds (VOCs) when the humid drying air is released from the process. According to the report by US EPA in 1995, the average amount of VOCs released from the lumber and wood industries were 41,423 tons per year in the United States (Beakler et al. 2005). Some of the

VOCs released were formaldehyde and methanol. These two are hazardous to both human's health and the environment (Milota 2006).

The main source of the VOCs is the extractives inside the wood (Beakler et al. 2005). The extractives, such as formaldehyde, methanol and terpenes, come to the surface along with the moisture during the drying process. Another source of VOCs beside the extractives is the break down product of bigger hydrocarbon molecules such as lignin and cellulose during the drying process.

It is not applicable to employ combustion-based systems such as a boiler incineration, regenerative thermal oxidation or a regenerative catalytic oxidation in order to destroy the VOCs from the exhaust air. Kiln drying operates in batch-mode, producing VOCs emission with great variation in concentration and volume, reducing the effectiveness of those systems (Shmulsky 2000). The application of activated carbon (AC) would need an additional treatment system in order to recover or eliminate the organic released during the regeneration process of the AC. Membrane technology is too costly to be applied and this technology needs additional pre-treatment before the exhaust air can be treated (Wang et al. 2001).

Another option for addressing the VOC emission is by removing the VOCs by condensation and recirculating the air within the kiln thus there is no exhaust air emitted. In such system, the hot air is passed through a heat exchanger (condenser) in order to cool down and to saturate the humid air, thus condensing part of the water vapour in the air. The air is recycled to the kiln drying after the condensate is removed. However, the VOCs, which were in the humid air, are now in the condensate. Therefore, the condensate needs to be treated before being discharge into the environment.

Presently, there is a guide for accessing the air quality for thermal processes in wood processing industries in New Zealand. However, it is likely that new and

stricter standards are going to be introduced, following the new standards in European Community (EC) by WHO (Metcalfe et al. 2008). Therefore, the existing wastewater treatment technologies will have their role in attempting to increase the effluent quality before being released to the environment. The treatment can utilize chemical, physical and biological means in order to achieve its goal.

1.3 Project Objectives

The main objectives of the research are:

1 To determine the condensate volume, contaminant identities (dissolved VOCs) and their concentration which come from the kiln-dried wood.

2 To measure the BOD, COD, TOC, DO, pH and other parameter of wastewater, in order to determine the appropriate treatment system.

3 To examine whether the trickling filter system has the potential to reduce the level of dissolved VOC, especially those that are dangerous for human health to an accepted value, or even complete removal.

4 To examine whether trickling filter using bark chips as a suitable support medium is able to treat the wastewater to meet the environmental regulations standards.

1.4 Hypothesis

1. VOC present in the condensate can be treated by trickling filter technology.
2. VOC level can be reduced to a level which is save to be discharged to fresh water source.

1.5 Research's Benefit

The benefits gained from this research are:

- Better understanding of the condensate characteristic produced from kiln-dried wood.
- The result of this research can be used in consideration of using trickling filter with bark chips in wood kiln drying industries and generally for industries with the same wastewater characteristic.

1.6 Thesis Scope and Organization

A summary of the current literature on the condition of the kiln exhaust air and the proposed treatment are presented in Chapter 2. Following the literature review, Chapter 3 describes the methodology and experimental procedures. The results of the experiments and discussion are presented in Chapter 4. The conclusions, followed by recommendations for future work are presented in Chapter 5 and 6.

Chapter 2 Literature Review

This literature review is done on the wood drying industry, in particular on radiata pine wood drying. Particular attention is given to the future problems that could arise based on the current environmental trends. Also, the present situation in the wood drying industry is discussed, in relation to the anticipated regulations. Trickling filter and activated sludge as the treatment options suitable for this particular application are reviewed and their limitations are discussed. The final section focuses on the wastewater treatment based on attached-growth microbial systems with organic matter as the support media.

2.1 Radiata Pine

Radiata pine is one of the main tree species used in New Zealand as a source of wood material. Radiata pine has many desirable properties. One desirable feature of the tree is its fast growth, providing there is a suitable environment. It is also a hardy tree and resistant to diseases. The wood has good properties which make it easy to be processed and suitable as a raw material for a diverse range of products, e.g. furniture for interior application, plywood, fibreboard, and particle board.

The wood from radiata pine is dominated by sapwood, the outer part of the log which has high moisture content between 100 – 220% on a dry basis. The heartwood, which is the core of the log, has lower moisture content, between 40 – 50%. The sapwood is highly permeable and dries rapidly, while the heartwood is less permeable, but since it has less moisture content, the drying time is also considerably shorter. The density of radiata pine is between 350 kg/m^3 for earlywood, which is part of the wood in the growth ring of a tree that is produced spring and summer, and 550 kg/m^3 for latewood, which grows in autumn and winter (Kininmonth et al. 1991), which grows in autumn and winter. This density range is categorized as medium density wood (Kininmonth et al. 1991).

2.1.1 Wood Composition and Structure

Wood is a composite material consisting of cellulose, hemicellulose, and lignin. Cellulose contributes to wood's tensile strength, while lignin provides mechanical support. The presence of lignin allows trees to grow very high without collapsing. Hemicellulose, together with pectin, embedded in the cell walls of plants, provides matrix for cellulose and lignin to form a cross-linking fibre in plants (Kininmonth et al. 1991) (Walker 2006).

Cellulose is the most important substance in wood. It contributes around 40 -45 % of cell wall in normal wood. Cellulose is a linear-chained polymer formed through a condensation reaction of glucose (Kininmonth et al. 1991) (Fig. 2.1) During the reaction, a glucose molecule is added to the polymer chain while removing one water molecule. Cellulose is a very large polymer with the average degree of polymerization of 10,000. The cellulose chains are held together along the chain direction by strong covalent bonds, while in the other two direction, there are relatively strong hydrogen bonds and weak van der Waals forces (Walker 2006).

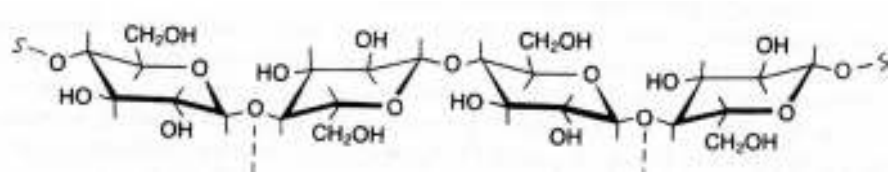


Figure 2.1 Structure of Cellulose (Walker 2006).

Hemicellulose is the name given to the polymer chain which consists of different, but closely related sugars. The polysaccharides are linked together the same way as the cellulose, but the chain is shorter and is branched (Fig. 2.2). The sugars involved are not only glucose but also other sugars such as mannose and xylose. The amount of hemicellulose and the structure and composition of individual hemicellulose vary between species, cell type and its location in the cell wall (Walker 2006). The function of hemicellulose in wood is still not known very

well. According to Keey (2000), it may be needed to form connections between the hydrophilic cellulose and the hydrophobic lignin, and by doing so, permit an effective transfer of shear stresses.

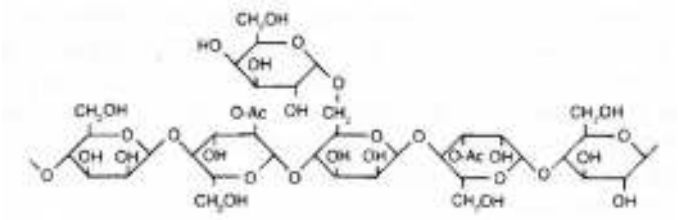


Figure 2.2 Partial chemical structure of O-acetyl-galactoglucomanan (a softwood hemicellulose)(Walker 2006).

Lignin is an aromatic and amorphous polymer that almost insoluble in many solvents (Fig. 2.3). It cannot be broken down to monomeric unit because, even when hydrolysed, it is very susceptible to oxidation and readily undergoes condensation reactions (Walker 2006). In the lignin structure, there are two types of cross-linking. The first linkage is C – O – C ether linkage and the other is C – C linkage. Lignin fills the space in the cell walls between cellulose and hemicellulose. It is covalently-linked to hemicellulose and therefore cross-links different polysaccharides, conferring mechanical strength to the cell walls in particular and to the plant as a whole. It is particularly abundant in the parts of plants that suffer from continuous mechanical stress such as branches where the lignin is formed below the bent part, pushing it up. This part is called compression wood.

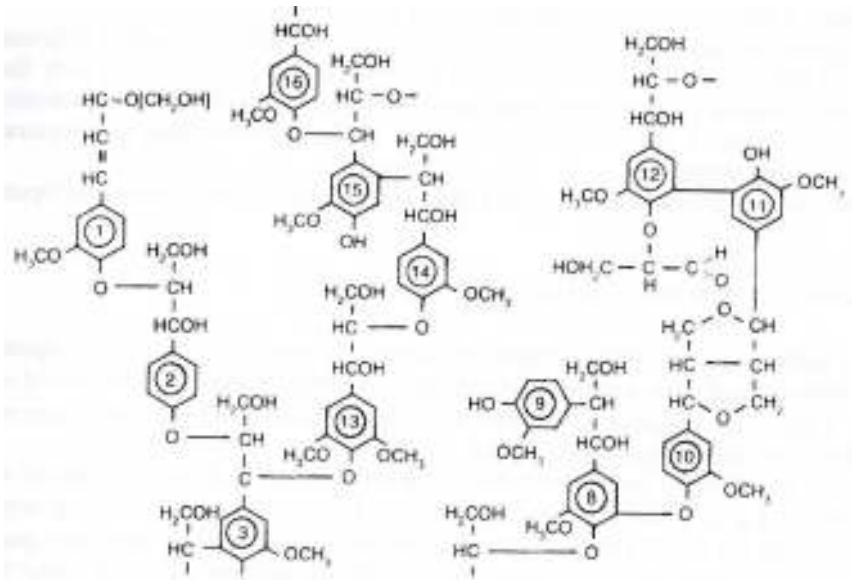


Figure 2.3 Partial chemical structure of lignin (Walker 2006).

The anatomical structure of radiata pine is basically similar to other conifers, however changes in cellular dimension occur because of different growth conditions, which later will have effect on the wood properties (Kininmonth et al. 1991). An electron micrograph scan (Fig. 2.4) show earlywood, latewood and resin canal. Earlywood is formed during the spring and summer. During this time, the vascular cambium develops into axially-elongated cells called tracheids with large central cavities with thin wall. The cell function is more for conduction of water than for support of the tree. In the opposite, during autumn and winter, the latewood is produced. The function of latewood is more for support than for water conduction (Walker 2006).

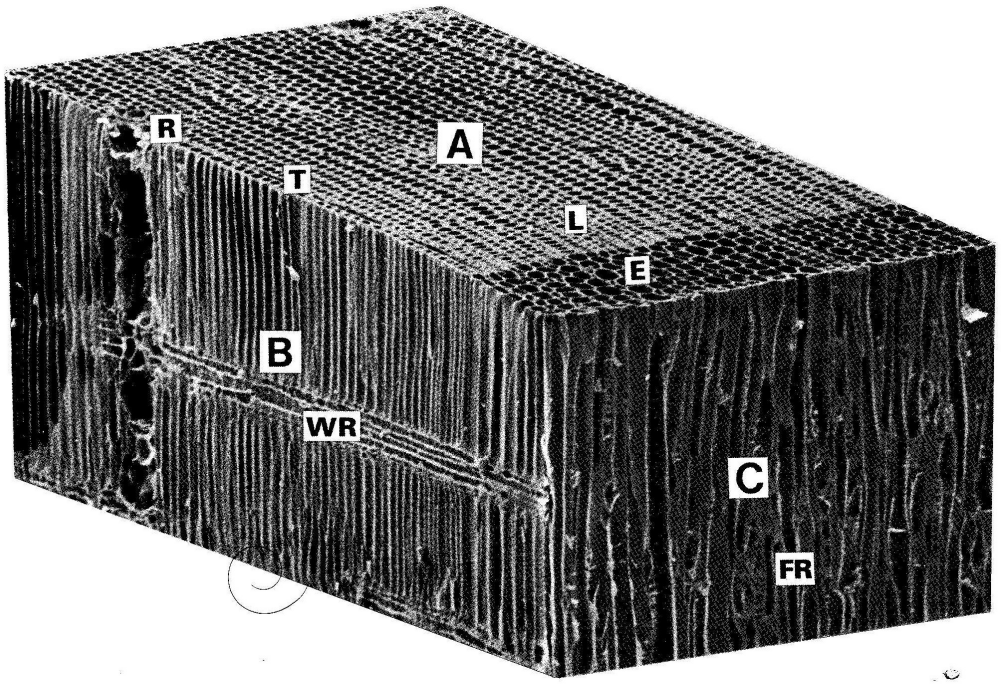


Figure 2.4 Scanning electron micrograph of radiata pine (Kininmonth et al. 1991).

Face A Transverse: T = cut ends of tracheids; L = latewood; E = earlywood; R = resin canal

Face B Radial/Longitudinal: WR = Wood Ray

Face C Tangential/Longitudinal: FR = fusiform ray

Radiata pine, which is considered a softwood, has a simple and uniform structure. According to Walker (2006), softwood is built up primarily of tracheids, providing both structural support and longitudinal conducting pathways in the wood. Tracheids tend to be longer in the lower levels in the tree compared to higher levels and also near the bark compared to the centre of the stem. The tracheids' wall is a composite structure made of a framework of long, slender microfibrils surrounded by hemicelluloses and bonded together by lignin, which provide structural rigidity (Slovak 2003). While the tracheids provide water conduction along the tree, bordered pits provide a passage for radial sap flow betweens cells.

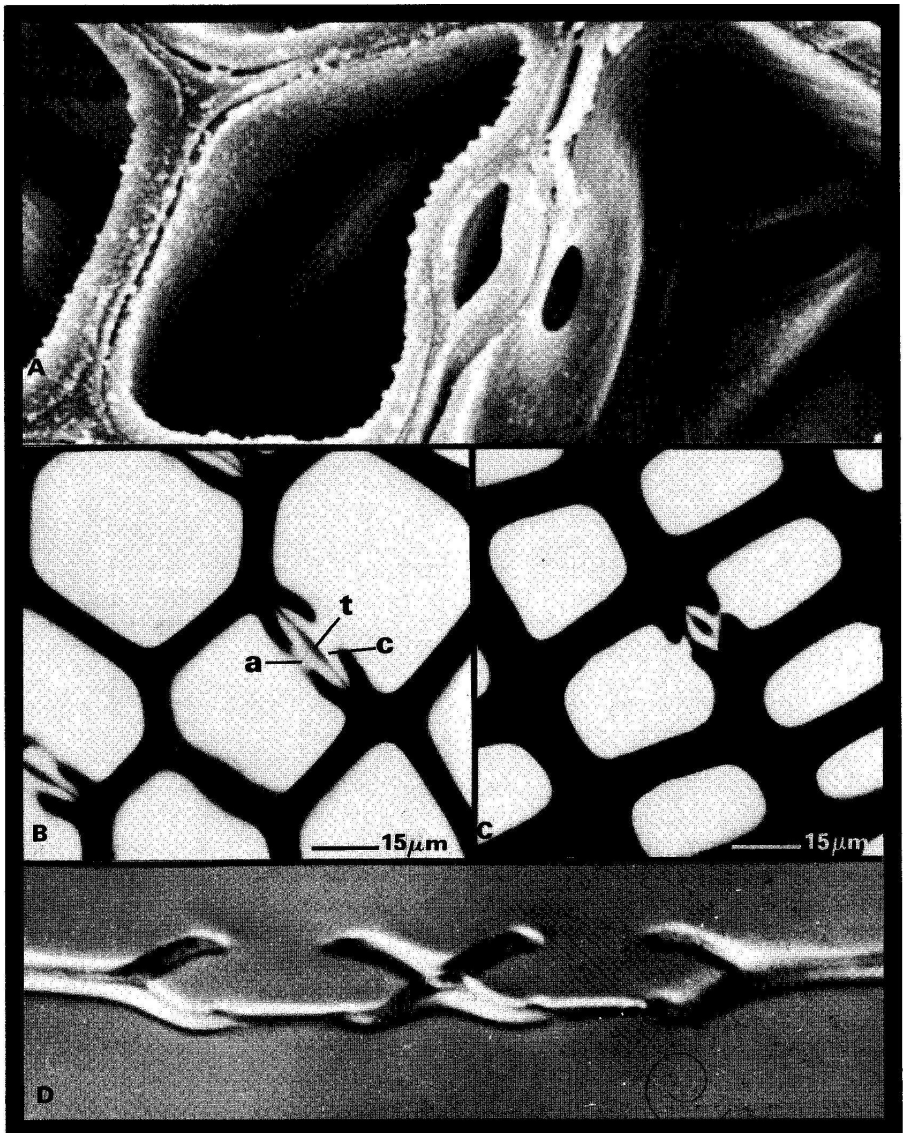


Figure 2.5 Pit structure on the cell walls (Kininmonth et al. 1991).

(A) Scanning electron micrograph of a bordered pit pair showing the pit aperture and transverse cut through the pit chamber

(B) Section through an earlywood bordered pit pair:
A = pit aperture; t = torus; c = pit chamber

(C) Section through a latewood bordered pit pair

(D) Aspirated earlywood pit pairs with tori closely pressed to the pit aperture

2.1.2 Moisture Movement in Wood

The movement of moisture in the wood is very important during the drying process. It is driven by the changes in moisture concentration. There are two main mechanisms of water movement in the wood: water diffusion and capillary flow. Both of them are controlled by the permeability of the wood and vapour pressure. I addition to the movement mechanisms, there are two types of moisture involved: free moisture and bound moisture

Diffusion is molecule movement through cell walls driven by a difference in vapour pressure, which in this case is due to the loss of moisture content in the wood. As the wood dries, the surface water is the first one to evaporate, therefore reducing the moisture content, which leads to the diffusion of water from the inner part of the wood. Diffusion occurs through cell walls. A capillary flow relies on the movement of moisture passing from cell to cell through pits.

The free moisture in the wood is evaporated relatively rapidly, and therefore creates a vapour pressure gradient, which leads to movement of bound moisture through diffusion. There are two kinds of diffusion that contribute to the bound moisture movement: Brownian diffusion and vacancy diffusion. Vacancy diffusion, according to Booker (1996), suggests that water molecules continuously pass through cell wall matrix by occupying and vacating sites within the matrix created by hydrophilic groups attached to the cell wall. The vacancy diffusion is illustrated in Figure 2.6.

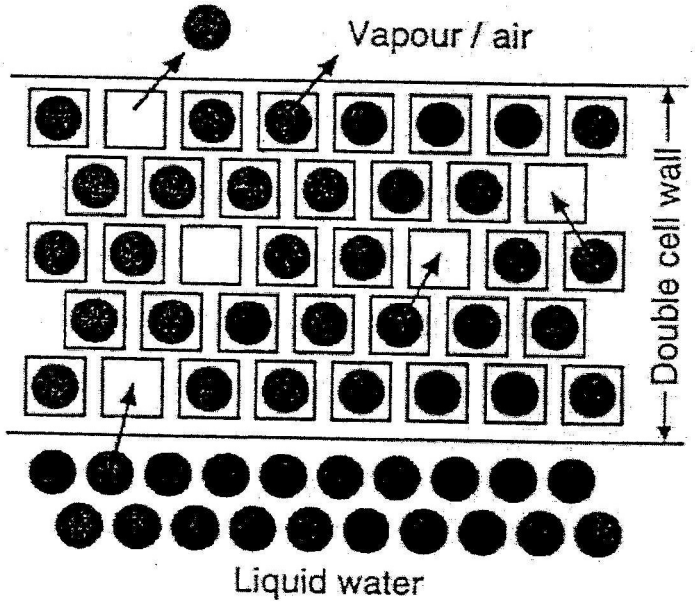


Figure 2.6 Vacancy diffusion (Booker 1996).

● = water molecules

□ = Vacant sites

⟶ = Movement of water molecules

2.2 Kiln Drying Technology

Kiln drying is one of two processes employed to produce dry wood product from green timber for furniture and building material. It most commonly used because of its known efficiency and advantages compared to ambient air drying. Wood drying by using kiln drying is much faster, a higher success rate for achieving the desired final moisture content and less variation in moisture content for the wood that is dried in the same schedule. Another advantage of kiln drying is the elimination of insect and fungal attack while the wood is dried compared to ambient air drying where the wood is exposed to the open atmosphere for long times.

The drying process applied to wood prior to chemical treatment has more advantages compared to stabilisation with only chemicals. The chemical treatment still leaves the wood susceptible to fungal growth over time. This is due to the

moisture content in the wood. The high moisture content, together with nutrients in the wood, provides an excellent environment for fungal growth. Using the drying process, the capability of the wood to resist such attack is increased, provided that the wood is not rewetted.

2.2.1 The Kiln Drying Process

In the kiln drying of timber, hot air removes the water present in the wood as water vapour. In the beginning, the heated air is blown into the wood chamber. The air transfers its heat into the wood and to the water on the surface. The water from the surface evaporates and results in low surface moisture. The moisture gradient between the surface and the core drives water to move from inside the wood to its surface.

During the drying process, the air becomes humid with the water evaporated from the wood. In order to maintain driving force for the evaporation of water from the wood, some of the humid air is released and fresh air is introduced into the process. The process is normally done automatically and depends on the wet bulb and dry bulb in the chamber. The commonly used wet bulb and dry bulb temperatures are between 40 to 140^{o}C and the difference between the wet bulb and dry bulb temperatures varies between 20 – 50^{o}C. The temperatures are chosen based on the quality and specification of the end product. Table 2.1 presents the information for different types of kiln drying processes that are used for drying wood.

Table 2.1 Kiln drying summary for 50mm thick lumber (Miller, 1992).

	Low Temperature Drying	Conventional Kiln	Accelerated Conventional Kiln	High Temperature Kiln
Dry bulb Temperature (^{o}C)	40 -60	70-80	80-100	120-140
Airflow (m/s)	1.5	3	4.5	5.0-8.0
Drying Time	15 days	5 days	2.5 days	13-20 hours
Minimum Final MC (%)	10-11	6	3	2
Capital Cost/m^3 dried	Low	High	Medium	Low
Production/dryer/year (m^3)	2000	3600	6000	18000
Operator Skill	Average	Skilled	Skilled	Skilled
Maintenance requirements	Low	High	High	Medium
Sterilises Lumber	No	Yes	Yes	Yes
Conditioning Period	Generally not required	Required (in kiln)	Required (in kiln)	Required
Stack Weighting - reduce distortion	No	Possible	Yes	Yes

A suitable drying schedule is needed in order to get a good result in term of strength and appearance. The schedules are made based on the types of the wood that are going to be dried, such as sapwood, heartwood, or mixed type, where one piece has both types. This is because parts of the tree have their own characteristics that require specific drying condition in order to get the best result. The pine grown in New Zealand has the tendency to shrink and twist within the first-ten growth rings. High temperature dying and stack-weighting are applied during the drying process in order to reduce the shrinkage and twist in the product. Figure 2.7 shows typical wood stacks used for drying.

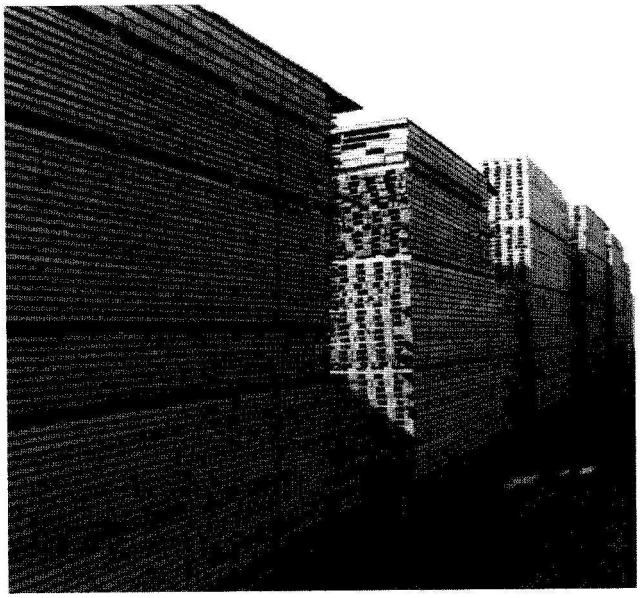


Figure 2.7 Wood stacks prior to drying (Walker 2006).

Most of the wood is dried soon after the cutting; therefore it does not require chemical treatment. In special cases, wood is treated and left outside for sometime. This will make the drying process more complicated and ends up giving a product with variable final moisture content.

2.3 Emissions from the Wood Drying Process

During the drying process, kilns release humid air. Besides water in the released air, unfortunately, some organic materials categorized as volatile organic compounds (VOCs) are also released. From US EPA data in 1995, the average amount of VOCs released from the lumber and wood industries to the environment is 41,423 tons per year in the United States (Beakler et al. 2005). Some of the VOCs such as formaldehyde and methanol are hazardous for both human health and the environment (Milota 2006).

There are three sources of VOC emissions during the drying process. The extractives in the wood itself, the reaction products produced in the wood during drying, and the reaction between gases emitted during the process. Extractives in

the wood, especially in conifers species, is one of the VOCs contributors for wood kiln-drying emission (Beakler et al. 2005). The extractives, such as formaldehyde, methanol and terpenes, come to the surface along with the moisture during the drying process.

During the drying process, reactions happen in the wood due to the change of moisture content and temperature. Acetic acid forms from the deacetylation/hydrolysis of the combined acetyl groups originally attached to the hemicellulose (Keey et al. 2000). The reaction is dependent on the buffering action, moisture content and temperature. The tannin and phenolic compounds in the wood also help to catalyze the auto-hydrolysis of the bound acetate. According to von Marutzky and Roffael (1977), some volatile substances, such as formaldehydes, come from thermal degradation of hemicelluloses and lignin. McDonald and Wastney (1995) analysed the volatile emission which is coming from high-temperature drying of radiata pine. (Table 2.2)

Table 2.2 Concentration of volatile emission arising from two high-temperature kiln schedule for *Pinus radiata* (McDonald et al. 1995).

Compound	Concentration (g/m^3) at dry/wet bulb temperatures	
	120/70	140/90
Formaldehyde	19.5	31
Acetic Acid	21.7	38.2
Monoterpenes	34.8	66.4
Hydroxylated Monoterpenes	12.6	1.7
Condenser Residues (resins and fatty acids)	16.4	16.4

VOCs, such as alcohols, aldehydes and acids also produced from the reactions among the gases present in the drying kiln during the process. These organic

compounds may not be present in the wood before drying, but when the wood is heated to a relatively high temperature, some of the volatile that also vaporize either react among themselves or break down to simpler organics. An example is the oxidation of α-pinene into ringed compounds containing aldehydes, ketones, and hydroxyl groups.

According to Slovak (2003), the measurement and identification of kiln emission using Selected Ion Flow Tube Mass Spectrometry (SIFT-MS) showed that acetaldehyde, ethanol, methanol, formaldehyde, and formic acid were present. Acetic acid was identified in all schedules except during the 90/50^{o}C. In addition to those VOCs, pinene was detected from drying with a dry/wet bulb temperature of 90/70^{o}C.

There are health and environmental concerns regarding some of those VOCs. Some of them are potential precursors of photochemical formation of ozone and other atmospheric oxidants and aerosols. In significant concentration, both acetaldehyde and formaldehyde have an adverse effect on human health, such as irritation of the eyes, respiratory tract and skin. In addition, formaldehyde is also known carcinogen. Methanol inhalation may cause blindness, headache, giddiness and insomnia. The exposure limit of some of these VOCs is presented in Table 2.3.

Table 2.3 Exposure limit of some VOCs present in the radiata pine (Anonymous 2004).

Compound	Exposure Limit (ppm)	Effect on Health
Methanol	200	Inhalation: Cough, dizziness, headache, nausea, weakness, visual disturbance.
		Skin: MAY BE ABSORBED! Dry skin, redness.
		Eyes: Redness, pain
		Ingestion: Abdominal pain, shortness of breath vomiting, convulsions unconsciousness. (Further see Inhalation).
Ethanol	500	Inhalation: Cough, headache, fatigue, drowsiness
		Skin: Dry skin
		Eyes: Redness, pain, burning
		Ingestion: Burning sensation, headache, confusion, dizziness, unconsciousness
Acetic acid	10	Inhalation: Sore throat, cough, burning sensation, headache, dizziness, shortness of breath, laboured breathing, lung oedema (symptoms my be delayed)
		Skin: Pain, redness, blisters, skin burns.
		Eyes: Redness, pain, severe deep burns, loss of vision.
		Ingestion: Abdominal pain, burning sensation, diarrhoea, shock or collapse, sore throat, vomiting.
Formic Acid	5	Inhalation: Sore throat, cough, burning sensation, headache, dizziness, shortness of breath, laboured breathing, lung oedema (symptoms my be delayed)
		Skin: MAY BE ABSORBED! Pain, blisters, serious skin burns.
		Eyes: Pain, redness, severe deep burns, blurred vision.
		Ingestion: Sore throat, burning sensation, abdominal pain, abdominal cramps, vomiting, diarrhoea.
Formaldehyde	0.3	Inhalation: Burning sensation, cough, headache, nausea, shortness of breath
		Eyes: Causes watering of the eyes, redness, pain, blurred vision.
Acetaldehyde	25	Inhalation: Cough
		Skin: Redness, pain
		Eyes: Redness, pain
		Ingestion: Dizziness, nausea, vomiting, diarrhoea.
Acetone	500	Inhalation: Sore throat, cough, confusion, headache, dizziness, drowsiness, unconsciousness.
		Skin: Dry skin
		Eyes: Redness, pain, blurred vision, possible corneal damage.
		Ingestion: Nausea, vomiting. (Further see Inhalation).

According to Keey, et al. (2000), in the United States, plant operators are subject to environmental audit. They must comply with the Clean Air Act and its amendments, with the limitation to the emission of VOCs, condensable organic vapours and particles less than 10 μm in diameter. The volatile organic emission are classified into Hazardous Air Pollutants (HAP), such as formaldehyde, which have threshold limit values for toxicity and substances reacted in the presence of sunlight to produce ozone(Bradfield et al. 1994).

2.4 Commercial Kilns and Laboratory Kilns

For this particular research, a laboratory kiln was used. According to Lavery and Milota (2000), the emissions from laboratory kilns are representative of commercial kilns. The results obtained from emission measurements of both a commercial kiln and a laboratory kiln are 0.87g of VOCs and 0.79g of VOCs per kg of oven-dry wood respectively. These results imply that laboratory kiln can represent commercial kilns at least in regards to mass generation. Therefore, a laboratory kiln can be used as an apparatus for investigating the emission from real kiln drying process. This is convenient in term of space and the amount of sample material used for every drying schedule. However, the research Lavery and Milota (2000) used Douglas-fir lumber, therefore further testing is required if other species of wood are used and it also depends on the setting of the system.

2.5 Treatment Technology

Some of the available technologies for reducing air emissions are combustion/oxidation, scrubbing, membrane technology, and biofilters. The choice of the treatment depends on the type of organics emitted and what type of production process is applied, batch or continuous.

Combustion technology uses the air that comes from the production process as combustion air. During the combustion, the organic materials and the particulate

matters are burnt. One example for this technology is incineration. The benefit of the combustion process is that it will give energy that can be used for steam generation, which can be used either for the main production process or to generate electricity. The application of combustion technology has been successful for veneer and strand dryers. However, it is not applicable to employ combustion-based systems such as a boiler incinerator, a regenerative thermal oxidizer, or a regenerative catalytic oxidizer for kiln driers. First, unlike the veneer and strand dryers, lumber kilns emit a variable amount of steam and VOCs during the process which decreases the operational efficiency of such system. In addition, the burner efficiency is influenced by the incoming air temperature which is the exhaust from the kiln (Shmulsky 2000). Finally, kiln drying process is a batch process, while combustion process is a continuous process. This difference in the operation method will result in larger costs because the combustion process as an end-of-pipe process has to be operated according to the kiln drying schedule.

The VOCs can be removed by absorption using activated carbon. This process is cheap and efficient. Activated carbon (AC) prepared by combining chemical and physical activation of olive stones is able to remove 9.76 g ethanol / 100 g AC (Silvestre-Albero et al. 2009). However, an absorption system using AC has some disadvantages. First, the air stream needs to be particulate-free in order to maximize the efficiency of its absorption capacity (Wang et al. 2001). Secondly, the AC needs to be regenerated regularly in order to remove absorbed VOCs. The regeneration is done by heating up the AC up to a certain temperature. The regeneration temperature depends on the type of organic absorbed and the characteristic of the AC used, e.g. 131^{o}C is the minimum desorption temperature for benzene in an AC with 2 nm diameter (Cheng et al. 2002). The main problem lies in the released organic contaminant during the regeneration process which needs additional treatment, if the organic is not going to be recovered. In addition, the regeneration incurs more cost. Thirdly, the effectiveness of the charcoal will

be reduced gradually every time it regenerated (Kim et al. 2006) (Silvestre-Albero et al. 2009).

A membrane separation process can remove the VOCs from the emitted air. The membrane works as a filter for the VOCs by separating the organic compound from the effluent air. In order to make sure that the process is working properly, some pre-treatment processes are needed, such as particulate removal and pH adjustment of the effluent. This technology works well in removing organics from the air. However, the cost involved in this particular process is very high (Wang et al. 2001).

Biofiltration is a known technology for treating industrial air emission. The process uses microorganisms attached to an appropriate medium to oxidise the organic materials from the stream, thereby reducing, or even removing all the organic content in the air stream. Bio filtration is a possible choice to treat the emissions from the wood kiln drying processes. The studies show that biofilters achieve efficiencies greater than 90% (Leson et al. 1992) (Le Cloirec et al. 2001) (Leson et al. 1993). However, the performance of the biofilter deteriorates because the filter beds are irreversibly affected by the accumulation of acetic acid and other toxic metabolites (Devinny et al. 1995; Leson et al. 1995). Besides that, for this particular process, the temperature of the exhaust air is still too high for the microorganism in the biofilm to withstand. The highest reported temperature for successful biofiltration is 72^{o}C, for the treatment of isobutyrate and 2-pentanone mixture in a batch process (Luvsanjamba et al. 2007). Kong (2001) studied the removal of methanol and α-pinene by using a biofilter with an operating temperature up to 70^{o}C. Cox (2001) treated ethanol vapors by using a thermophilic biotrickling filter at temperatures up to 53^{o}C.

The problem of high temperatures exhaust from kiln-drying can be solved by adding a heat exchanger to cool down the air, producing condensate which contains organic compounds. The cooled-down air therefore can be circulated

back to the kiln since it is freed from some of the water and organic matter. The recycle of treated exhaust air instead of using a fresh air will save some cost on heating because the treated exhaust air temperature is higher than ambient air temperature. Besides that, there will be no emission from the kiln during the drying process since there is no air released to the atmosphere.

The no-emission system above can easily cope up with the regulation on air quality standard in New Zealand. Presently, the National Ambient Air Quality Standards 2004 and National Ambient Air Quality Guidelines 2002 have become the reference for the industry in New Zealand in assessing their emissions in order to apply for consents. However, there is an indication that these guidelines and standards may change and become stricter in the future. This indication comes from the revision of the WHO guidelines on air quality in Europe and some of the materials are not covered by New Zealand standards or guidelines, such as the $PM_{2.5}$ and NO_2 (Metcalfe et al. 2008).

Even though the system does not produce air emission, it still produces condensate as an effluent that needs to be treated before it is released. The existing wastewater treatment technologies will have a role in attempting to increase the effluent quality. Since it is expected that the organic contaminants that presents in the condensate are easily-biodegraded organic compounds, the removal attempts will be conducted using the traditional trickling filter technology.

2.5.1 Trickling Filter

Trickling filter (TF) technology is used extensively to treat wastewater that originates from both residential and industrial processes. TF is an attached growth process. In this process, carbonaceous organic matter in the wastewater provides an energy source for the production of new cells for a mixed population of microorganisms. The microbes convert carbon into cell tissue and oxidized end products that include carbon dioxide and water. The microorganisms form a layer

called a biofilm. The treatment occurs as the liquid flows over the biofilm. The biofilm is attached on a bed of support media. The TF is very efficient with respect to adhesion of bacteria, contact between water and biofilm and reaeration of the water (Henze et al. 1995)

In this process, the wastewater typically goes through a primary sedimentation process before it is distributed over the gravel bed, trickles down to be collected under the filter and flows to a secondary tank. Aeration is provided through natural drafts resulting from the temperature difference between the ambient and the internal air. Operation of the TF can vary: single pass, alternating double-filtration and recirculation mode (Bitton 1994).

TF filter designs are classified by hydraulic or organic loading rates (Tabel 2.4) (Metcalf et al. 2003). Rock filter designs have been classified as low- or standard-rate, intermediate-rate, and high rate. Plastic packing is used typically for high-rate designs, but it also has been used for lower organic loading.

Table 2.4 Trickling filter classification (Metcalf et al. 2003).

Design Characteristic	Low or standard rate	Intermediate Rate	High rate	High Rate	Roughing
Type of packing	Rock	Rock	Rock	Plastic	Rock/plastic
Hydraulic loading ($m^3/m^2.d$)	1 – 4	4 – 10	10 – 40	10 – 75	40 – 200
Organic loading (kg $BOD/m^3.d$)	0.07 - 0.22	0.24 - 0.48	0.4 - 2.4	0.6 - 3.2	>1.5
Recirculation ratio	1	0 - 1	1 - 2	1 - 2	0 - 2
Filter flies	Many	Varies	Few	Few	Few
Sloughing	Intermittent	Intermittent	Continuous	Continuous	Continuous
Depth (m)	1.8 – 2.4	1.8 – 2.4	1.8 – 2.4	3.0 – 12.2	0.9 – 6
BOD removal Efficiency (%)	80 – 90	50 – 80	50 – 90	60 – 90	40 – 70
Effluent quality	Well nitrified	Some nitrification	No nitrification	No nitrification	No nitrification
Power ($kw/10^3\ m^3$)	2 – 4	2 – 8	6 – 10	6 – 10	10 – 20

As with other treatment systems, TF has advantages and disadvantages. Some advantages of TF are ease of operation, low maintenance, and energy cost due to the natural aeration, and able to withstand shock loads. Disadvantages include filter clogging which happens for continuous high organic loads, flies, and potential odour problem caused by the anaerobic region formed in the treatment process.

TF is chosen as the treatment in this research instead of AS system because of the assumption of low concentration of contaminant (below 1000 mg/L of COD). This assumption is made based on the low concentration of VOC in the exhaust air. This assumption was supported by McDonald et al. (1999). They reported that the average COD from condensate collected from a vacuum drying process of radiata pine was 815 mg/L. The value obtained from the kiln drying process may differ since there is possibility that not all the water and organics are condensed. However, Xin (personal communication, May 2007) reported COD value of 260 mg/L in the condensate came from a kiln dryer.

However, TF is sometimes less efficient than other treatment systems especially activated sludge (AS), such as TF is reported to be less reliable compared to AS, more expensive and have poorer performance in cold weather. Some of the issues are driven by propagation of myths as much as by data analysis and factual determinations (Parker 1999).

The first issue is that TFs are less reliable compared to AS. This conclusion is based on the result of the effluent of the process. However, the poor result of a conventional TFs is due to the poor performance of the secondary sedimentation design (Parker 1999). The common design flaw is the higher surface overflow rates and lower sidewater depths. Matasci et al. (1988) report that with the replacement of secondary clarifier with a deeper flocculator clarifier, the effluent suspended solid (ESS) drops from 25 mg/L to 18 mg/L. The application of this

method to a rock filter plant is able to reduce the initial value of ESS and BOD value between 20 and 45 mg/L to less than 10 mg/L (Norris et al. 1982).

The second issue which is a commonly faced by TFs is that the process performs poorly in cold weather, but this is not supported by a general fact. According to Parker et al (1999), this opinion is derived from rock TFs that often suffer in winter months. The uncovered rock TFs are subject to excessive cooling with cold ambient temperature as the ventilation is usually unrestricted and units are operated essentially as cooling towers. Moreover, the rock TFs are typically shallower than modern plastic media units. However, when plastic media TFs have their ventilation rate controlled and are covered; the temperature drop is usually less than $2^{o}C$ in winter months. It is also reported that when the temperature drop from 20.2 to $13.8^{o}C$, the reaction rates in nitrifying trickling filters (NTFs) fall 24 % while when using a commonly accepted design equation for nitrifier growth rate (Anonymous 1993), an AS process rates are predicted to decline 47 % over the same temperature range (Parker et al. 1995).

Another common myth about TFs is that they are expensive compared to the AS process. This idea is derived from low-rate rock filters which require massive structure and land compared to AS technology. However, it is not possible to generalize this for all situations.. There are numerous published examples where TFs have proven less costly than conventional AS processes (Fedotoff et al. 1982) (Hyde et al. 1984) (Gorder et al. 1990) (Parker et al. 1989) (Parker et al. 1994) (Parker et al. 1998).

2.6 Biofilm

The biofilm is the substance responsible for the contaminant removal in a trickling filter. The biofilm is formed by inoculating the trickling filter with a solution containing certain microorganisms which feed on the contaminant. The type of

microorganism introduced to the system is chosen based on the contaminant that will be treated by the system.

Microorganisms form a biofilm in order to attach on a support medium. According to Logan et al. (1988), microorganisms attach to the surfaces and to other microorganisms throughout nature and engineered system. This is due to the help of the extracellular polymeric substances (EPS) which are produced by the microorganism for attaching itself to the surrounding substratum as slime (Higgins et al. 1997). EPS are the main component of a biofilm's organic mass. In general, biofilm contains of 95 % water and 5 % dry material; and approximately 90% of the organic carbons is EPS (Characklis et al. 1990).

The porosity of a biofilm plays an important role on the removal process. Higher porosity resulted in better removal, because high porosity gives better mass transfer between the wastewater and the biofilm. The porosity of a biofilm changes with the thickness. Zhang et al (1994) measured that the porosity of an outermost layer and an innermost layer of a biofilm are 84-93% and 58-67% respectively, when grown from a 350-700 mg/L COD feed stream. This means as biofilms become denser, the pore volume becomes smaller through the biofilm depth (Boltz et al. 2006).

Biofilm production is influenced by the dissolved oxygen (DO) concentration and nutrients. La Motta (2003) reported that at low DO concentration, the production of EPS was very low. The production of new biofilm happens on the outermost layer, since it is subjected to the highest concentration of DO and substrate (Boltz et al. 2006).

2.7 Bark Chips as Support Media

The support media used in the experiment is bark chips. Bark chips are chosen because, even though it is an organic material, they are stable. Beside that, there

are various microorganisms present on the bark chips naturally, which can be used to treat the organic contaminant in the wastewater. Bark chips are cheap abundant, and easy to replace since they are considerably lighter than rocks. The used bark chips can be used for soil amendments (Harkin et al. 1971).

There has been some research in wastewater treatment that used wood based product, such as wood chips and barks. Jones Saliling (2007) used wood chips and wheat straw as an alternative support media in biofilter to treat wastewater. Cropsey and Weswig (1973) used douglas-fir bark as support media for a trickling filter and found that bark chips were superior to rock for support media.

Chapter 3 Methods and Materials

3.1 Wastewater Characterisation

The condensate from the Fogarty pilot-scale kiln was characterised for its contaminant concentration and the amount of condensate produced during the drying process. It was considered that the condensate production profile for the period of drying is compulsory to estimate the loading of the treatment system proposed. In order to obtain the data, the discharge of the condenser was collected and analysed periodically.

The wastewater was created in the laboratory by drying radiata pine lumber using the Fogarty Kiln Dryer. The lumber was dried to a moisture content of 10-14 %. The vapour produced was condensed and analysed for organic content by using Gas Chromatography (GC) and also analysed for its Chemical Oxygen Demand (COD) value and Biological Oxygen Demand (BOD) value.

3.1.1 Lumber Preparation

This section describes the method of preparing radiata wood samples for kiln drying operation and samples for measuring the final moisture content of the drying result.

Equipment: table saw, plastic bag (for lumber), plastic rope.

Steps:

1. 16 pieces of green lumbers, 5 cm x 10 cm x 200 cm were selected from Sutherland and Co. Ltd. Sawmill, Kaiapoi, Canterbury, New Zealand.
2. Each piece was subdivided into 6-8 pieces, first with sample 40 cm in length followed by a sample 2-3 cm in length. All samples were labelled. (Fig. 3.1)

Figure 3.1 Wood Piece Labelling.

3. The 2-3 cm samples were separated from the 40 cm samples.
4. The long samples were placed in bags and stored in a cool room (-5 ^{o}C) until drying.
5. The 2-3 cm specimen was analysed immediately in order to obtain the initial moisture content (IMC) and oven dry density (ρ_{od}).

3.1.2 Measurement of Lumber Density, and Moisture Content (Using 2-3 cm Specimen)

This section describes the method of obtaining the variables used in calculation of the final moisture content of the drying result.

a. Green Weight Measurement

Equipment: Balance

Steps:

1. The balance was turned on.
2. The scale was set to zero.
3. The sample was put on the balance.
4. The value was recorded.

b. Volume Measurement

Equipment: Beaker glass, balance

Steps:

1. The balance was turned on.
2. A 2 L glass beaker was filled with water until about 75 % full.
3. The beaker was put on a weighing scale.

4. The weighing scale was set to zero
5. The sample was forced into the water-filled beaker until all the surfaces were submerged.
6. The weight shown by the balance was recorded.
7. The volume of the sample is the same as the weight, assuming that the density of water is 1000 kg/m^3.

Note: Step 5 and 6 were done quickly to minimise the impact of water absorption.

c. Dry Weight Measurement

Equipment: balance

Steps:

1. The oven temperature was set to 103^oC.
2. The samples were put in the oven.
3. The samples were left in the oven for 48 hours.
4. The samples were taken out from the oven
5. The weight of the samples was measured immediately.

d. Wood Density and Initial Moisture Content (MC) Determination.

Steps:

1. The density (ρ) the oven dry wood was calculated based on its dry weight (DW) and volume (V).

$$\rho_{oven\text{-}dry}\ (kg/m^3) = DW\ (kg) / V\ (m3)$$

2. The initial moisture content (IMC) of the samples was based on its green weight (GW) and dry weight (DW).

$$IMC\ (\%) = (GW\ (kg) - DW\ (kg)) / DW\ (kg) \times 100\%$$

Note: The density value was used for measuring the final moisture content of the lumber samples after drying process.

3.1.3 Lumber Drying and Condensate Collection

This section covered the method for the drying process operation, condensate collection and final moisture content measurement of the drying result.

a. Lumber Drying

Equipment: Fogarty tunnel drying, data logger (computer)

Steps:

1. The computer was started up
2. The Advantech Genie Data Acquisition and Control program was activated. This program was used in order to monitor the temperature along the drying tunnel.
3. The kiln dryer was turned on.
4. The fan speed was set to 4 out of 10. The setting depended on the desired initial wet-bulb temperature (60^{o}C). The air velocity was measured using a portable anemometer.
5. The temperature was set to the 80^{o}C. The heater temperature was adjusted together with the cooling water opening to get the initial dry-bulb temperature.
6. The kiln was let to run until it reached a steady state.
7. The drying chamber was opened.
8. The logs were put in certain order.
9. The chamber door was closed.
10. After 24 hours, the temperature of the chamber was monitored closely in order to get the desired final moisture content.
11. the drying process was stopped

Figure 3.2 Fogarty Kiln Dryer.

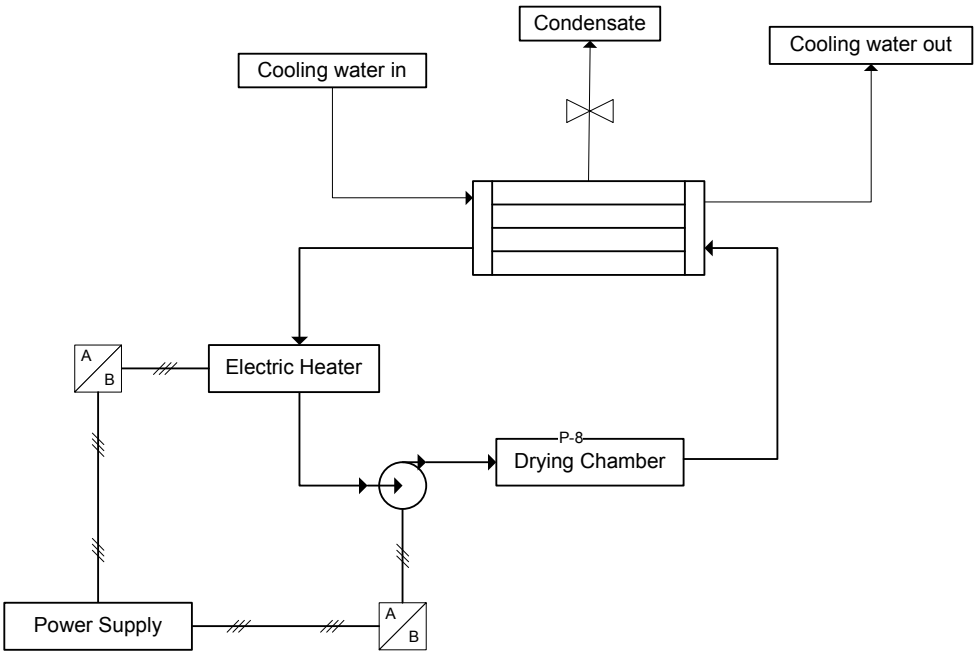


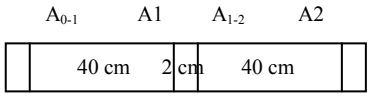
Figure 3.3 Fogarty Kiln Dryer Diagram.

b. Moisture Content Measurement for the Kiln-Dried Wood

Equipment: Wagner MMC 220 Extended Range moisture meter

Steps:

1. By using the density calculated from the small specimens, the average density of each lumber samples is calculated
   For example:



$$\rho_{A1} = \frac{(\rho_{Ao-1} + \rho_{A1-2})}{2}$$

2. The average density was input as a parameter for the moisture meter.
3. The density of the lumber was measured by putting the moisture sensor in the back moisture meter on the lumber surface.
4. Step number 2 and number 3 were repeated for each lumber samples.

c. Condensate Collection

Equipment: 1 L Plastic bottles, 1 L measuring cylinder, Filter Paper

Steps:

1. During the drying process, the condensate was drained from the condenser every an hour during the experiment. The time of collection between samples was increased to every two hours when the amount of condensate produced was small e.g. less than 1 L in 2 hours
2. The condensate volume was measured using a 1 L measuring cylinder.
3. The condensate was filtered using Whatman 41 filter paper to remove the solid debris in the condensate.
4. The condensate was analysed for its Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), and the concentration of organic contaminants by means of Gas Chromatography. If immediate

analysis was not available, the sample was stored in a plastic bottle and stored in a freezer at -20^{o}C.

3.2 Treatment

This section described the method of preparing bark chips media for the trickling filter, pump characterization, and trickling filter characterization and main treatment operation.

3.2.1 Pre-treatment Experiment

a. Wood Bark Preparation

This step was done in order to get bark chips with desired size to be used as the biofilm support media.

Equipment: Alko Dynamic H 2200 S Grinder, sieving plate

Steps:

1. The wood bark chips were grinded. The wood bark chip was obtained from Crusaders Garden Makers, Sockburn, Christchurch, New Zealand.
2. The wood bark flakes resulted from the grinder were sieved based on the desired particle size.
3. The chosen particle sizes for the experiment were 2.8 – 4 mm and 5.6 – 8 mm.
4. The bark chips were put into a re-sealable plastic bag for storage before use.

Figure 3.4 Wood bark Chips used in the treatment. This bark chips average diameter of 5.6 – 8.0 mm.

b. Peristaltic Pump Characterization

The different peristaltic pumps were calibrated. The results were used during the experiment n determining the organic release from bark chips (section 3.2.1 point e), column adsorption capacity (section 3.2.1 point g), and bio-trickling filter treatment (section 3.2.2)

Equipment: peristaltic pump, measuring cylinder, stop watch, 1 L beaker glass

Steps:

1. 1 L The beaker glass was filled with water.
2. The Masterflex L/S precision standard drives with 10-turn speed control and remote capabilities peristaltic pump, HV-77521-57 (1 – 100 rpm) with Neoprene tube number 17 and HV-77521-47 (6 – 600 rpm) with neoprene tube number 14 were set up.
3. The intake side of the tube used to pump the water was put inside the beaker.
4. The output side of the tube was put inside a measuring cylinder.

5. The scale on the peristaltic pump was set to the desired value.
6. The pump was started.
7. The stopwatch was started when the water started to fill the measuring cylinder.
8. After the water level reached a certain value, the pump was stopped as well as the stopwatch.
9. The reading on the measuring cylinder (ml), the stopwatch (s), and the scale used on the pump used during the measurement were noted.
10. The flow rate (Q) was calculated by using the formula:

$$Q_{water} = \frac{V}{t}$$

11. The Q was plotted against the scale on the pump

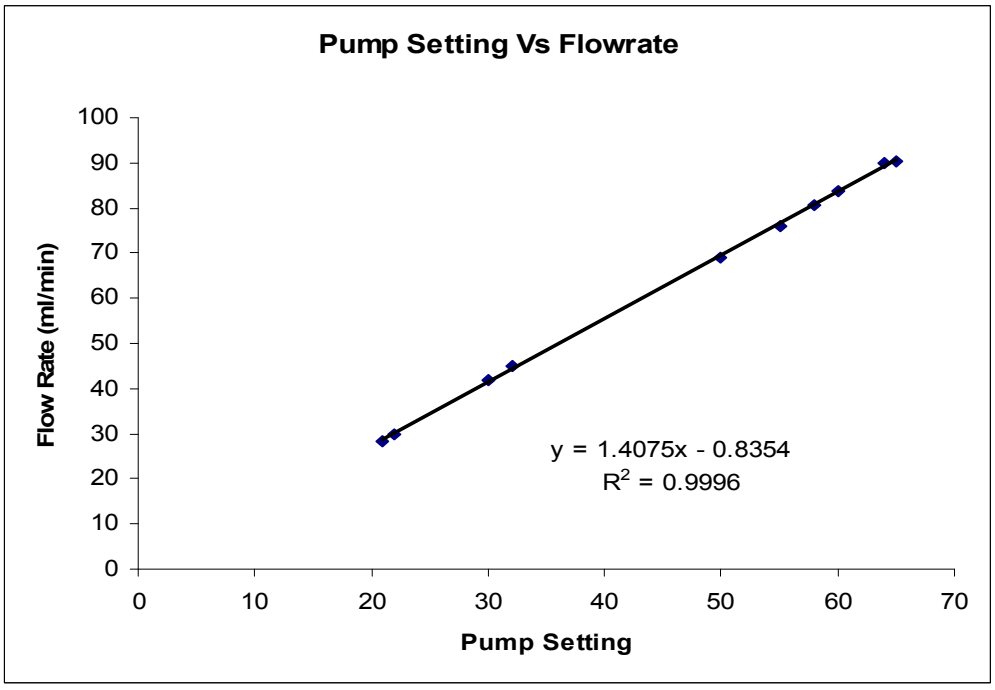


Figure 3.5 6 – 600 rpm Masterflex peristaltic pump flow rate calibration curve using HV 07014 - 20 head and norprene tube (propylene-based material) no. 14.

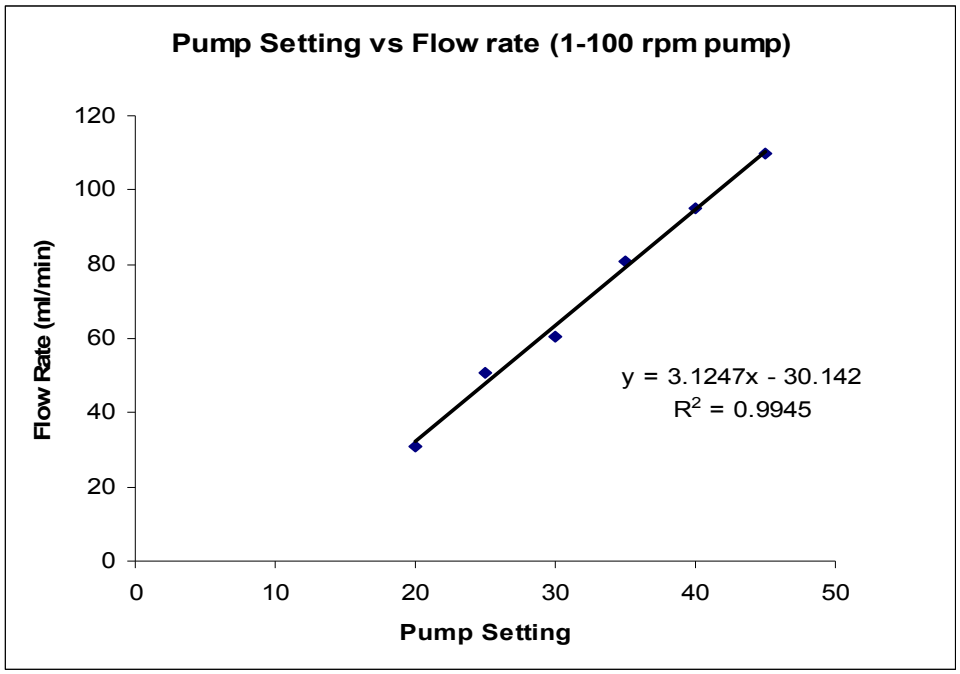


Figure 3.6 1 – 100 rpm Masterflex peristaltic pump flow rate calibration curve using HV 07017 - 20 head and norprene tube (propylene-based material) no. 17.

c. Bed Residence Time

The residence time in the column with different bark chip size as well as flow rate was measured.

Equipment: plastic column, wood bark chips, peristaltic pump, stopwatch, stand, clamp, beaker.

Steps:

1. The wood bark chips were put into the column (D = 3 cm, h = 35 cm) until the bed height was 30 cm.
2. The column was attached to the stand by means of a clamp.
3. The beaker was filled with water.
4. The pump was set up to certain scale reading in order to obtain the desired flow rate (Q_1), based on the result of Q–pump scale plot (see Section 3.2.1.b)

5. The intake side of the tube was put into a water-filled beaker.
6. The output side of the tube was put on top of the column.
7. The pump was started. The water from the beaker was pumped into the column. The pumping was done for approximate 10 minutes in order to let the column achieve its steady state condition.
8. The pump was turned off and at the same time collect the water that come out from the column.
9. The volume of the water collected is measured (V_1).
10. The superficial flow rate is calculated by using the following equation:

$$U_0 = \frac{Q_1}{(\pi \times r^2)}$$

Where: U_0 = Superficial Velocity (cm/min)
Q_1 = pump flow rate (ml/min)
r = column diameter (cm)

11. The residence time is calculated by using the following equation:

$$t = \frac{V_1}{Q_1} \times 60$$

Where: t = residence time (s)
V_1 = volume of water collected (ml)
Q_1 = pump flow rate (ml/min)

d. Bed Void Fraction Determination.

This experiment measured the percentage of the void in the bark chips bed, depended on the bark size.

Equipment: plastic column, wood bark flakes, measuring cylinder, stand, clamp.

Steps:

1. The wood bark flakes density (ρ_b) was determined by dividing a bark sample mass with its volume. The volume is measured using the method for measuring the volume of wood sample (section 3.2.1 point b)
2. The empty column mass was measured (M_1)
3. The column is filled with bark flakes until the bark bed height is 30 cm.
4. The column with the bark flakes bed was weighed (M_2).
5. The difference between M_1 and M_2 is the bed weight (ΔM).
6. The actual bed volume is calculated by the following equation:

$$V_b = \frac{\Delta M}{\rho_b}$$

Where: V_b = actual bed volume (cm^3)
ΔM = bed mass (g)
ρ_b = bark density (g/cm^3)

7. The void fraction was calculated by the following equation:

$$\varepsilon_b = \frac{V_c - V_b}{V_c}$$

Where: ε_b = bed void fraction
V_c = column volume with height of 30 cm (cm^3)
V_b = actual bed volume (cm^3)

e. Organic Release from Bark Chips

This experiment was done in order to obtain the knowledge whether the bark used as the bed in this experiment would release the extractives contained into the wastewater which pass through. The extractives release may give false reading about the amount of organic contaminants removed by the process.

Equipment: Water supply tank, peristaltic pump, wood bark flakes.

Steps:

1. The 100 L tap water supply tank was filled with water.
2. The column (D = 3 cm, h = 35 cm) was attached to a rig by means of clamps.
3. Freshly ground bark was put into the column until the bed height was 30 cm.
4. The pump was set to a flow rate of 20 ml/min and started.
5. The samples from both inlet and outlet of the column were taken twice a day and analysed for its COD content.

f. Artificial Wastewater Supply

The wastewater from the kiln drying contained some organic solvents. However, the two dominant solvents present in the wastewater were methanol and ethanol. Formaldehyde was not included even though it is a major concern and very soluble in water. This was because the peak that represented formaldehyde did not appear in the chromatographs of the condensate samples. There were some possible explanations that it was not detected. For instance, it is readily oxidized by the atmospheric oxygen to be formic acid. Besides that, formaldehyde has a very low boiling point (-21^{o}C), which also made it less soluble in water during the condensation. Since the process to obtain the wastewater was quite expensive and time consuming, it was decided to use artificial wastewater which consisted of tap water supplemented with methanol and ethanol. The concentration used were based on the analysis of the condensate (see Section 3.1.3.c)

Material: Water, methanol 99.8 %, ethanol 99.7 %

Equipment: Measuring cylinder, beaker glass, volumetric flask, wastewater supply tank

Steps:

1. Using a measuring cylinder, 3.2 ml of methanol was measured.

2. Using a measuring cylinder, 8.3 ml of ethanol was measured.
3. The combination of the above was called 1x concentration.
4. Both methanol and ethanol were mixed and diluted to 1 L.
5. The 1 L solution was put into 100 L supply tank and diluted to 100 L with tap water
6. The solution was mixed before being pumped into the treatment column.

g. Column Absorption Capacity

This experiment was done in order to obtain the knowledge whether the Perspex column used in this experiment absorbed some of the organic contaminants. The organic absorption by the column may give false reading about the amount of organic contaminants removed by the process. In this experiment, sodium hydrazine was added to the artificial wastewater with final concentration of 0.1 part per million (ppm) to prevent any biological activities to interfere with the artificial wastewater concentration.

Equipment: Artificial wastewater, wastewater supply tank, peristaltic pump, plastic column, glass beads.

Steps:

1. Glass beads with size of 2 - 4 mm were separated from the random size glass beads by using sieving tray.
2. The glass beads were put inside the column.
3. The wastewater in was pumped into the column.
4. The 10 ml samples of the inlet and outlet of the column were collected twice a day.
5. The inlet and outlet COD values were determined.
6. The artificial wastewater was added until the outlet COD value was steady.

3.2.2 Bio-trickling Filter Treatment

Equipment: Water supply tank, peristaltic pump, wood bark flakes, artificial wastewater.

Steps:

1. The 100 L tap water supply tank was filled with artificial wastewater (see Sec. 3.2.1.f).
2. The column (D = 3 cm, h = 35 cm) was attached to a rig by means of clamps.
3. Freshly ground bark was put into the column until the bed height was 30 cm.
4. The pump was set to certain flow rate and started.
5. The samples from both inlet and outlet of the column were taken twice a day and analysed for its COD content.
6. The experiments were carried out using variations on the contaminant concentration and flow rate as in Table 3.1

Table 3.1 Experiment Variations.

Barks Chip Size (mm)	Concentration	Flow rate (ml/min)
2.8 - 4.0	1x	20
5.6 - 8.0	1x	20
5.6 - 8.0	2x	20
5.6 - 8.0	4x	20
5.6 - 8.0	8x	20
5.6 - 8.0	16x	20
5.6 - 8.0	1x	30
5.6 - 8.0	1x	40
5.6 - 8.0	1x	50
5.6 - 8.0	1x	60

3.3 Analysis Method and Standard

This section covered all the analysis procedures used in during the experiments.

3.3.1 Total Organic Carbon Analysis Method

Total Organic Carbon (TOC) analysis was performed using the combustion – infrared method. The Analysis was performed by means of Apollo 9000 TOC Analyser with STS 8000 autosampler, by Teledyne Tekmar, with the help of TOC Talk Software. The instrument was located in the Environmental Laboratory, Civil and Natural Resources Engineering, University of Canterbury, Christchurch New Zealand.

a. TOC Analysis

Equipment: Apollo 9000 TOC Analyser with STS 8000 autosampler, 40 ml Volatile Organic Analysis (VOA) vials,

Steps:

1. The TOC analysis instrument was started and left for 15 – 20 minutes in order to reach the optimum pressure and temperature (900^{o}C) for TOC analysis.
2. The TOC Talk software was started.
3. 30 ml of each sample were put into the VOA vials.
4. The VOA vials was put in the autosampler tray.
5. Through the TOC Talk control screen, the TOC analyser was set for the sequence of samples, and number of injection.
6. The analysis was started.

b. TOC Standard Solution

Equipment: balance, 500 ml beaker, 250 ml measuring cylinder, spatula, 1000 ml volumetric flask.

Steps:

1. 2.948 g of citric acid, $C_6H_8O_7$ was dissolved in 250 ml of DI water.
2. The solution was diluted to 1000 L in a volumetric flask.

Note: This is a 1000 mg C/L standard solution. In order to make standard solution with a different concentration, the solution is diluted accordingly. The standard curve was plotted by analysing standard solution in different concentration.

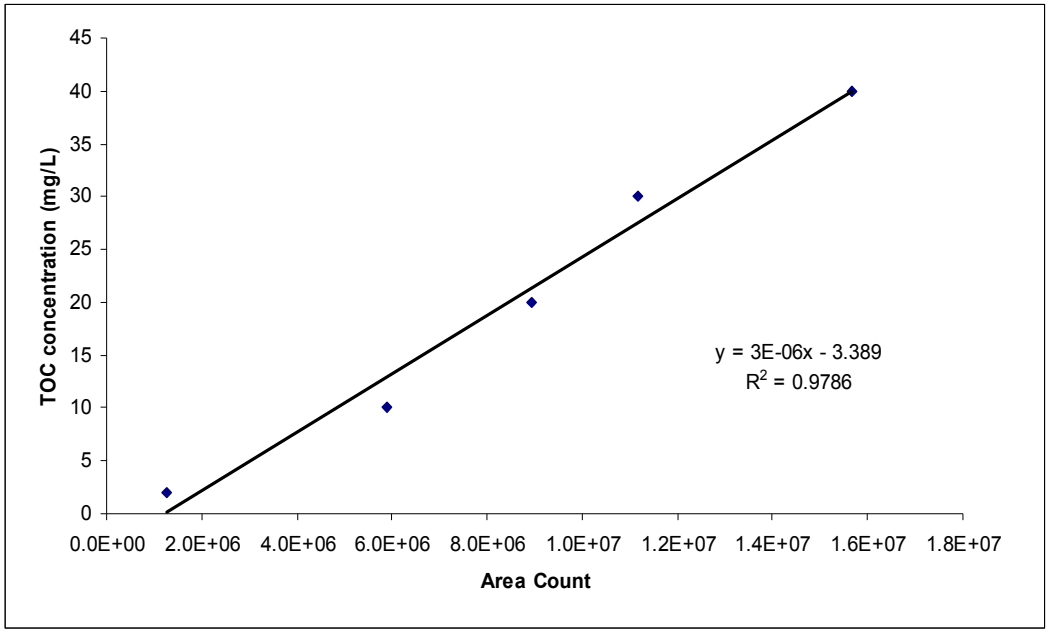


Figure 3.7 TOC calibration curve.

3.3.2 Chemical Oxygen Demand Analysis Method

This section covered the Chemical Oxygen Demand analysis method, including the preparation of the reagents needed.

a. Sulphuric Acid Reagent

Equipment: balance, 50 ml beaker, spatula.

Steps:

1. 25.3 g of silver sulphate (Ag_2SO_4) was added to 2.5 L concentrated sulphuric acid.
2. The solution was left for 48 hours in order to let the silver sulphate dissolve.

b. Reagent A

Equipment: balance, 50 ml beaker, 250 ml measuring cylinder, spatula, 1000 ml volumetric flask.

Steps:

1. 10.21 g of potassium dichromate ($K_2Cr_2O_7$), 33.3 g of mercury sulphate ($HgSO_4$) and 167 ml of sulphuric acid were added to 500 ml of DI water.
2. The solution was diluted into 1000 ml in a volumetric flask.

c. COD Digestion Reagent

Equipment: 250 ml and 500 ml measuring cylinder, 500 ml glass bottle, magnetic stirrer, cooling bath.

Steps:

350 ml of sulphuric acid reagent (section 3.3.1 point a) was slowly added to 150 ml of reagent A (section 3.3.1 point b) in a 500 ml glass bottle while the bottle was in a cooling bath and the magnetic stirrer was active.

d. COD Sample Preparation

Equipment: *MF-millipore membrane, mixed cellulose esters, Triton free, 0.45 μm*, *25 mm* filter paper, *MF-millipore membrane, mixed cellulose esters, Triton free, 0.22 μm*, *25 mm* filter paper. vacuum pump, *Buchner* funnel, 11 ml vials, Vivaspin 4 centrifuge filter with 5000 molecular weight cut-off (MWCO), Heraeus 3L centrifuge

Steps:

- Filtering used membrane filter:
  1. The filtering apparatus was set up: Buchner funnel, vacuum pump and the membrane filter.
  2. The samples were filtered and stored in the vials.
- Filtering used centrifuge filter
  1. The sample was put into Vivaspin 4 centrifuge filter with 5000 molecular weight cut-off (MWCO) and centrifuged using Heraeus 3L centrifuge.
  2. The samples were filtered and stored in the vials.

e. COD Digestion Procedure

Equipment: COD digestion tubes, 5 ml volumetric pipette, Hach DR/2000 Spectrophotometer, Hach Digital Reactor Block 200 (DRB 200),

Steps:

1. The Hach Digital Reactor Block 200 (DRB 200) was turned on and set up for COD digestion (150^{o}C, 2 hours)
2. The instrument was left around 15 minutes in order to heat up until 150^{o}C
3. 2 ml of COD reagent was measured by using a volumetric pipette and was put into a 10 ml COD digestion tube.
4. 5 ml of a sample was measured by using a volumetric pipette and was put into the COD digestion tube.

5. The cap was put on and tightened firmly and the COD digestion tube was shaken.
6. The COD digestion tube was put into the Hach Digital Reactor Block 200 (DRB 200) and the process was started by pressing the START button.

f. COD Value Analysis

Equipment: Hach DR/2000 Spectrophotometer

Steps:

1. The digestion tube was taken out from the reactor and left to cool down until approximately 20^{o}C
2. Hach DR/2000 Spectrophotometer instrument was started by pressing the ON button and left for 15 minute to stabilize.
3. The instrument was set to read COD up to 1200 mg/L by activated custom programme #951 and the wavelength was set to 620 nm.
4. The digestion tube surface was wipe clean by using tissue to make sure the correct reading was obtained.
5. The digestion tube was put into the measuring chamber in the spectrophotometer instrument and the COD value (mg/L) was noted.

3.3.3 Biological Oxygen Demand Analysis Method

This section covered the preparation of the reagents used in BOD analysis as well as the analysis procedure. The BOD analysis was done as per BOD standard analysis 5210D Proposed Respirometric Method and using *Hach BODTrak* Instrument. The solution involved the preparation of nutrient solution, standard solution for BOD analysis, blank and wastewater sample.

a. Potassium Hydroxide, 6 N

Equipment: balance, 100 ml beaker, 100 ml volumetric flask, 100 ml glass bottles

Steps:

1. 33.6 g of KOH was diluted in 70 ml of DI water by using beaker glass and manually stirred until dissolved.
2. The solution was diluted further in a 100 ml volumetric flask and stored in a 100 ml glass bottle.

b. Phosphate buffer solution, 1.5 N

Equipment: balance, 100 ml beaker, 100 ml volumetric flask,100 ml glass bottles

Steps:

1. 20.7 g of NaH_2PO_4 was diluted in 70 ml DI water by using beaker and stirred using magnetic stirrer.
2. The pH was adjusted to 7.2 using the KOH 6 N (see Sec. 3.3.2 point a)
3. The solution was diluted further in a 100 ml volumetric flask and stored in a 100 ml glass bottle.

c. Ammonium Chloride Solution, 0.71 N

Equipment: balance, 100 ml beaker, 100 ml volumetric flask, 100 ml glass bottles

Steps:

1. 3.82 g of NH_4Cl was diluted in 70 ml of DI water by using beaker and manually stirred.
2. The pH was adjusted to 7.0 using the KOH 6 N (see Sec. 3.3.2 point a)

3. The solution was diluted further in a 100 ml volumetric flask and stored in a 100 ml glass bottle

d. Calcium Chloride solution, 0.25 N

Equipment: balance, 100 ml beaker, 100 ml volumetric flask, 100 ml glass bottles

Steps:

1. 3.66 g of $CaCl_2.2H_2O$ was diluted in 70 ml of DI water by using beaker and manually stirred.
2. The solution was diluted further in a 100 ml volumetric flask and stored in a 100 ml glass bottle.

e. Magnesium Sulphate solution, 0.41 N

Equipment: balance, 100 ml beaker, 100 ml volumetric flask, 100 ml glass bottles

Steps:

1. 10.1 g of $MgSO_4.7H_2O$ was diluted in 70 ml of DI water by using beaker and manually stirred.
2. The solution was diluted further in a 100 ml volumetric flask. And stored in a 100 ml glass bottle.

f. Ferric Chloride solution, 0.018 N

Equipment: balance, 100 ml beaker, 100 ml volumetric flask, 100 ml glass bottles

Steps:

1. 0.484 g of $FeCl_3$ was diluted in 70 ml of DI water by using beaker and manually stirred.

2. The solution was diluted further in a 100 ml volumetric flask and stored in a 100 ml glass bottle.

g. Alkaline solution, 1 N

Equipment: balance, 100 ml beaker, 100 ml volumetric flask, 100 ml glass bottles

Steps:

1. 4 g of NaOH was diluted in 70 ml of DI water by using beaker and manually stirred.
2. The solution was diluted further in a 100 ml volumetric flask and stored in a 100 ml glass bottle.

h. Sodium Sulphite Solution, 0.025 N

Equipment: balance, 100 ml beaker, 100 ml volumetric flask, 100 ml glass bottles

Steps:

1. 0.1575 g of Na_2SO_3 was diluted in 70 ml of DI water by using beaker and manually stirred.
2. The solution was diluted further in a 100 ml volumetric flask and stored in a 100 ml glass bottle.

Note: This solution had to be prepared fresh every time before use.

i. Trace Solution

Equipment: balance, 1000 ml beaker, 1000 ml volumetric flask, magnetic stirrer, 1000 ml glass bottles

Steps:

1. 40 mg $MnSO_4.4H_2O$, 57 mg H_3BO_3, 43 mg $ZnSO_4.7\ H_2O$, 35 mg $(NH_4)_6Mo_7O_{24}$, 100 mg Fe-Chelate were put together and diluted in 800 ml DI water by using beaker and stirred using magnetic stirrer.
2. The solution was diluted further in a 1000 ml volumetric flask. And was stored in a 1000 ml glass bottle.
3. The solution was sterilized at 120^oC and pressure of 200 kPa for 20 minutes by using autoclave.

j. Glucose-Glutamic Acid Solution

Equipment: balance, 500 ml beaker, 1000 ml volumetric flask 1000 ml glass bottles, magnetic stirrer.

Steps:

1. 50 g of glucose powder and 50 g of glutamic acid powder were dried 103^oC for 1 hour
2. 15 g of each was taken from the dried powders and dissolved into 300 ml of DI water by using beaker and stirred using magnetic stirrer.
3. The solution was diluted using 1000 ml volumetric flask stored in a 1000 ml glass bottle. The solution was stored up to 1 week

k. BOD Standard Solution

Equipment: 1000 ml volumetric flask, volumetric pipettes

Steps:

1. A 1000 ml volumetric flask was filled with approximately 800 ml of DI water.
2. 10 ml of glucose-glutamic acid solution (see Sec. 3.3.3. point j) was measured using a volumetric pipette and was put into the volumetric flask

3. 6 ml of phosphate buffer solution (see Sec. 3.3.3 point b)) was measured using a volumetric pipette and was put into the volumetric flask.
4. 2 ml of NH_4CL solution (see Sec. 3.3.3 point c) was measured using a volumetric pipette and was put into the volumetric flask.
5. 2 ml of $CaCl_2$ solution (see Sec. 3.3.3 point d) was measured using a volumetric pipette and was put into the volumetric flask.
6. 2 ml of $MgSO_4$ solution (see Sec. 3.3.3 point e) was measured using a volumetric pipette and was put into the volumetric flask.
7. 2 ml of $FeCl_3$ solution (see Sec. 3.3.3 point f) was measured using a volumetric pipette and was put into the volumetric flask.
8. 2 ml of trace solution (see Sec. 3.3.3 point i) was measured using a volumetric pipette and was put into the volumetric flask.
9. The volumetric flask was filled with DI water until 1000 ml

l. Blank Solution

Equipment: 1000 ml volumetric flask, volumetric pipettes

Steps:

1. A 1000 ml volumetric flask was filled with DI water until the volume was approximately 800ml.
2. 4 ml of phosphate buffer solution (see Sec. 3.3.3 point b) was measured using a volumetric pipette and was put into the volumetric flask.
3. 2 ml of NH_4Cl solution (see Sec. 3.3.3 point c) was measured using a volumetric pipette and was put into the volumetric flask.
4. 2 ml of $CaCl_2$ solution (see Sec. 3.3.3 point d) was measured using a volumetric pipette and was put into the volumetric flask.
5. 2 ml of $MgSO_4$ solution (see Sec. 3.3.3 point e) was measured using a volumetric pipette and was put into the volumetric flask.

6. 2 ml of $FeCl_3$ solution (see Sec. 3.3.3 point f) was measured using a volumetric pipette and was put into the volumetric flask.
7. 2 ml of trace solution (see Sec. 3.3.3 point i) was measured using a volumetric pipette and was put into the volumetric flask.
8. The volumetric flask was filled with DI water until 1000 ml

m. Sample Solution

Equipment: 1000 ml volumetric flask, volumetric pipettes, 250 ml measuring cylinder.

Steps:

1. A 100 ml sample was measured using 250 ml measuring cylinder.
2. The sample pH was adjusted using the alkaline solution (see Sec. 3.3.3 point g) until the pH was 7.0.
3. The sample was put into 1000 ml volumetric flask and diluted 1000 ml with DI water.
4. A 180 ml of diluted sample was taken using 250 ml measuring cylinder
5. 0.4 ml of $Cacl_2$ solution (see Sec. 3.3.3 point d) was measured using a volumetric pipette and was put into the volumetric flask.
6. 0.4 ml of $MgSO_4$ solution (see Sec. 3.3.3 point e) was measured using a volumetric pipette and was put into the volumetric flask.
7. 0.4 ml of $FeCl_3$ solution (see Sec. 3.3.3 point f) was measured using a volumetric pipette and was put into the volumetric flask.
8. 0.4 ml of trace solution (see Sec. 3.3.3 point i) was measured using a volumetric pipette and was put into the volumetric flask.
9. 0.06 ml of phosphate buffer solution (see Sec. 3.3.3 point b) was measured using a volumetric pipette and was put into the volumetric flask.
10. The solution was filled using the diluted sample (step 3) until the volume was 200 ml.

n. *Hach BODTrak* Operation Procedure.

Equipment: *BODTrak* instrument, *BODTrak* sample bottles, *BODTrak* seal cap, 25 ml measuring cylinder, 250 ml measuring cylinder, incubator.

Steps:

1. The samples were heated or cooled until the temperature was 18 – 22^{o}C.
2. 145 ml of a sample solution (see Sec. 3.3.2.1.11**)** was measured by using a measuring cylinder and was put into a *BODTrak* sample bottle.
3. 15 ml of a seed solution was measured by using a measuring cylinder and was put into the *BODTrak* sample bottle above.
4. A 3.8 cm magnetic stirrer bar was put into each *BODTrak* sample bottle.
5. Stopcock grease was applied to the lip of the bottle and to the top of the seal cup to provide a seal.
6. The seal cup was placed in the neck of the bottle.
7. A sodium hydroxide granule was put into the seal cup. The sodium hydroxide was not allowed to fall into the sample.
8. The bottles were placed on the chassis of the *BODTrak*. The bottle was connected to an appropriate tube, based on the chassis and tube number, and the cap was tightened firmly.
9. The *BODTrak* was put into an incubator which has been set to temperature of 20 $\pm$ 1^{o}C.
10. The *BODTrak* instrument was connected to the power supply and turned ON.
11. Correct stirrer bar operation was confirmed in each bottle.
12. The test duration was selected by simultaneously pressing and holding the < (left) and > (right) arrow keys until the time menu appeared.
13. The channel 6 key was pressed to activate the test length parameter.
14. The arrow key was used to choose the 5-days test.

15. The OFF button was pressed to save the selection and exit the menu.
16. In order to start a test, the channel number corresponded to the bottle was pressed.
17. The ON key was pressed to display the choices of BOD range.
18. The > (right) arrow key was pressed once to choose the 350 mg/L BOD range.
19. The ON key was pressed and held in order to start a test. The test was started when the display showed the graph for the corresponding bottle.
20. The BOD result of each bottle was directly read from the display by pressing the corresponding number.

Note: The glucose-glutamic acid standard solution (see Sec. 3.3.2 point k) was used for check whether the instrument worked properly in place of sample. DI water was used for blank solution, instead of the sample (see Sec. 3.3.2 point l).

3.3.4 Gas Chromatography (GC) Analysis Method

Equipment: *Varian Cp* 3800 Gas Chromatography Instrument, Varian Cp 8410 auto-injector instrument, volumetric pipette, 9 mm glass vial (index no. 32009-1232).

Steps:

1. 1 – 1.5 ml of each samples were put into glass vials by means of volumetric pipette.
2. The vials were put into the GC auto-injector tray.
3. The helium, dry air and nitrogen gas flow to the GC were turned ON.
4. The computer was turned ON and Varian system control programme (ver. 6.30) was activated.
5. The GC was turned ON.

6. The *Chrompack capillary column, CP-sil 5CB* column temperature was set to 80^{o}C.
7. The FID detector was activated and the temperature was set to 200^{o}C.
8. The auto-injector volume was set to 1 μl.
9. The injector point temperature was set to 220^{o}C.
10. The analysis time was set.
11. The set up was saved as a custom method for later use.
12. A new samples list was created in order to do automatic injection. The list contained the name, number of repeated injection, and position of the samples in the auto-injector tray
13. The folder to save the result of analysis was set.
14. The analysis method was set (see no. 9)
15. The auto-injection was begun. The result can be review from the saved file.

3.3.5 Ethanol and Methanol Standard Solution for Gas Chromatography

a. Ethanol Standard Solution

Equipment: Volumetric pipette (1 ml and 5 ml), , 1000 ml volumetric flask, 100 ml volumetric flask, 100 ml glass bottles.

Steps:

1. The 1000 ml volumetric flask was filled with approximately 500 ml DI water
2. 6.35 ml of ethanol 99.7 % was put into the volumetric flask by means of volumetric pipette.
3. The volumetric flask was filled with DI water until 1000 ml. This is ethanol solution with concentration of 5000 mg/L
4. 100 ml volumetric flask was filled with approximately 50 ml of DI water.
5. 1 ml of ethanol 5000 mg/L was put into the 100 ml volumetric flask.

6. The flask was filled with DI water until 100 ml. This is ethanol standard solution of 50 mg/L

Note: In order to make standard solution with a different concentration, adjust the volume of ethanol 5000 mg/L accordingly.

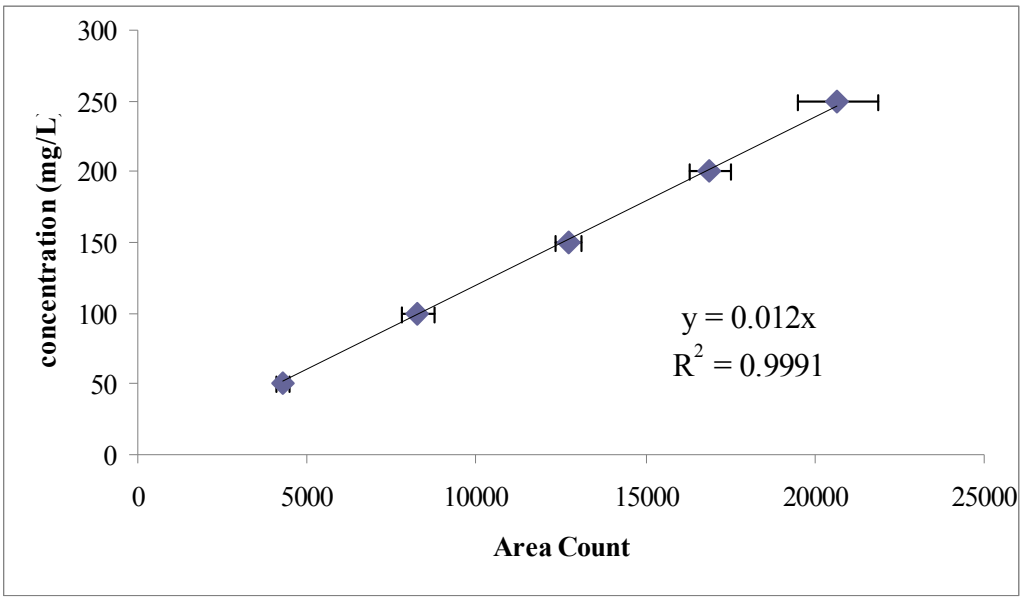


Figure 3.8 Ethanol standard curve for relating ethanol concentration in water to peak area for 1μL injection on the GC.

b. Methanol Standard Solution

Equipment: Volumetric pipette (1 ml and 5 ml), 1000 ml volumetric flask, 100 ml volumetric flask, 100 ml glass bottles.

Steps:

1. The 1000 ml volumetric flask was filled with approximately 500 ml DI water
2. 6.35 ml of methanol 99.5 % was put into the volumetric flask by means of volumetric pipette.

3. The volumetric flask was filled with DI water until 1000 ml. This is methanol solution with concentration of 5000 mg/L
4. 100 ml volumetric flask was filled with approximately 50 ml of DI water.
5. 1 ml of methanol 5000 mg/L was put into the 100 ml volumetric flask.
6. The flask was filled with DI water until 100 ml. This is methanol standard solution of 50 mg/L

Note: In order to make standard solution with a different concentration, adjust the volume of methanol 5000 mg/L accordingly.

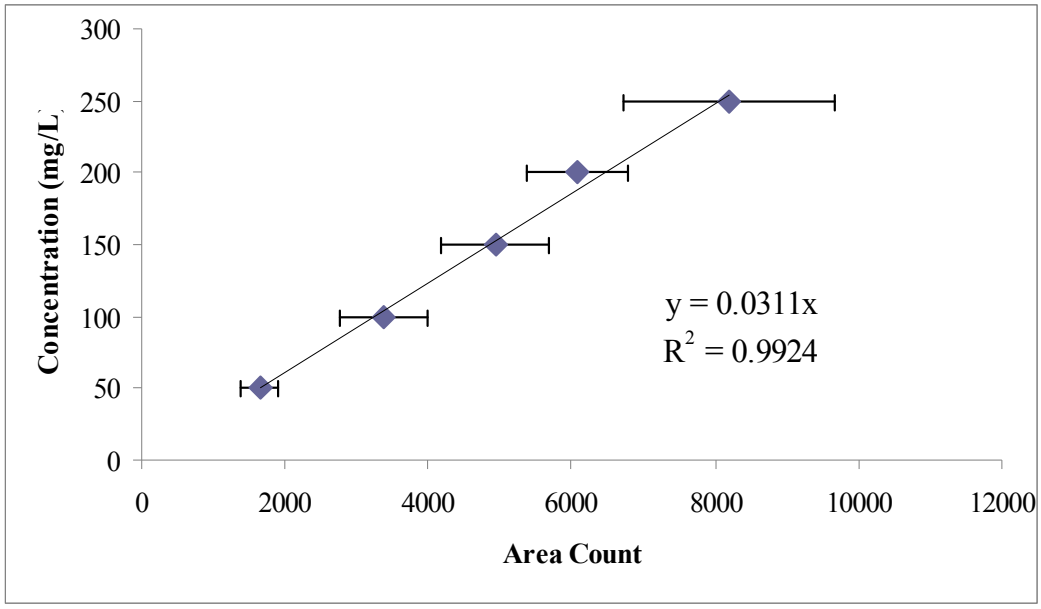


Figure 3.9 Methanol standard curve for relating methanol concentration in water to peak area for 1μL injection on the GC.

3.3.6 Ammonia Content Analysis by using Kjeldahl Method

a. Selenium Catalyst for Kjedahl Digestion

Equipment: Balance, 100 ml beaker, glass bottle

Steps:

1. 2.5 g of selenium oxide (SeO_2)was weighted.
2. 100 g opf potassium sulphate (K_2SO_4)was weighted.
3. 20 g of copper sulphate pentahydrate ($CuSO_4.5H_2O$) was weighted.
4. All the powder was mixed together.

b. Sodium Hydroxide Solution 30% m/v (g/L)

Equipment: Balance, beaker, 100 ml volumetric flask

Steps:

1. 3 g of sodium hydroxide granules was weighed.
2. The sodium hydroxide was mixed with approximately 50 ml of DI water.
3. The solution was put into the volumetric flask.
4. The solution was diluted until 100 ml.

c. Sodium Hydroxide Solution 0.01 N

Equipment: Balance, beaker, 100 ml volumetric flask

Steps:

1. 0.04 g of sodium hydroxide granules was weighted.
2. The sodium hydroxide was mixed with approximately 50 ml of DI water.
3. The solution was put into the volumetric flask.
4. The solution was diluted until 100 ml.

d. Hydrochloric Acid Solution 0.1 N

Equipment: volumetric pipette (1 ml), 100 ml volumetric flask

Steps:

1. The volumetric flask was filled with approximately 70 ml of DI water.

2. 1 ml of hydrochloric acid 1 N solution by means of volumetric pipette and it was put into the flask.
3. The solution was dilluted until 100 ml.

e. Total Nitrogen Analysis by Means of Kjeldahl Method

Equipment: 25 ml volumetric cylinder, 100 ml beaker, 100 ml volumetric flask, 500 ml Kjedahl flask, 500 ml distillation flask, 100 ml conical flask, 25 ml burette

Steps:

1. Turn ON a heating mantle and set the temperature between 370 – 410^{o}C.
2. 0.51 g sample was weighed. For blank, the sample addition was omitted.
3. 0.2 g of selenium based catalyst was weighed.
4. 25 ml of concentrated sulphuric acid was measured by means of volumetric cylinder.
5. The sample, catalyst and the sulphuric acid was put together into the Kjedahl flask.
6. The Kjedahl flask was heated up in the heating mantle until the solution become bright green.
7. The flask was cooled naturally in ambient air temperature.
8. The digested solution was diluted into 100 ml in a volumetric flask.
9. 5 ml of the diluted solution was put into 250 ml distillation flask.
10. 5 ml of sodium hydroxide 30 % m/v (see Sec. 3.3.5 point b) was also put into the distillation flask.
11. A distillation system was set up, the system included a condenser which was used to condensed the ammonia released during the distillation.
12. 25 ml of hydrochloric acid 0.1 N was put into a 100 ml conical flask to gather the distillate.

13. The distillation process was run for approximately 10 min.
14. The distillate was back-titrated by using sodium hydroxide solution 0.01 N until the pH of 7 was reached. The pH was measured by means of pH meter *Eutech intrument P_h510*.
15. The amount of 0.01 N NaOH from the titration was noted.
16. The ammonia content was calculated using this formula:

$$C_{NH_3} = \left(Vt_{blank} - Vt_{sample}\right) \times C_{NaOH}$$

Note: C_{NH3} = Ammonia Concentration.

Vt_{blank} = Volume of 0.01 N NaOH used for blank titration.

Vt_{sample} = Volume of 0.01 N NaOH used for sample titration.

C_{NaOH} = NaOH concentration, which is 0.01 N

Chapter 4 Results and Discussion

4.1 Drying Process

Condensate was produced using the pilot-scale Fogarty kiln dryer in the Chemical and Process Engineering Department, University of Canterbury, New Zealand (Fig. 4.1). The kiln system consisted of an air-heating chamber, drying chamber, and condensation chamber. Initially, the air passed through the air-heating chamber to increase the temperature. The heated air was blown into the drying chamber where the drying took place. After that, the air passed through the condensation chamber where the vapour condensed and separated from the air. In the condensation chamber, the air was passed through pipes that were submerged underwater. The water was changed continuously to ensure the heat transfer from the hot air in the pipes to the water. In the experiment, the air temperature exiting the condensation chamber was $55 \pm 3^{o}C$. The air that went through the condensation chamber was directed back to the air-heating chamber to raise the temperature again. The kiln was modified by putting temperature probes in several spots to observe the temperature changes throughout the system. The temperatures obtained from these probes were recorded digitally.

Figure 4. 1 Fogarty kiln dryer used for production of condensate from drying radiata pine.

During the drying process, a dry-bulb/wet-bulb temperature of approximately 80/60^{o}C was desired. In order to get the desired temperature, the heater controller was adjusted to get an initial dry-bulb temperature of 80^{o}C. The actual temperature was slightly above 80^{o}C due to the limitation of the control system. After the first half of the drying process (~ 15-20 hours), the dry-bulb started to increase (Fig 4.2). This condition happened due to the amount of water that could be evaporated from the samples was not as much as the first half. This resulted in less heat transfer due to evaporation and subsequently less heat removal during condensation. The excessive heat transfer to the air caused a higher dry bulb temperature. In order to maintain the dry-bulb temperature at approximately 80^{o}C, the heat input from the heater was reduced. The wet-bulb temperature profile increased during the first 10 hours of the run.. The increase was due to the water evaporating from the samples, raising the relative humidity of the circulating air. After the first 10 – 15 hours, the wet-bulb/dry-bulb temperature difference remained roughly constant, indicating an approximately constant relative humidity in the chamber.

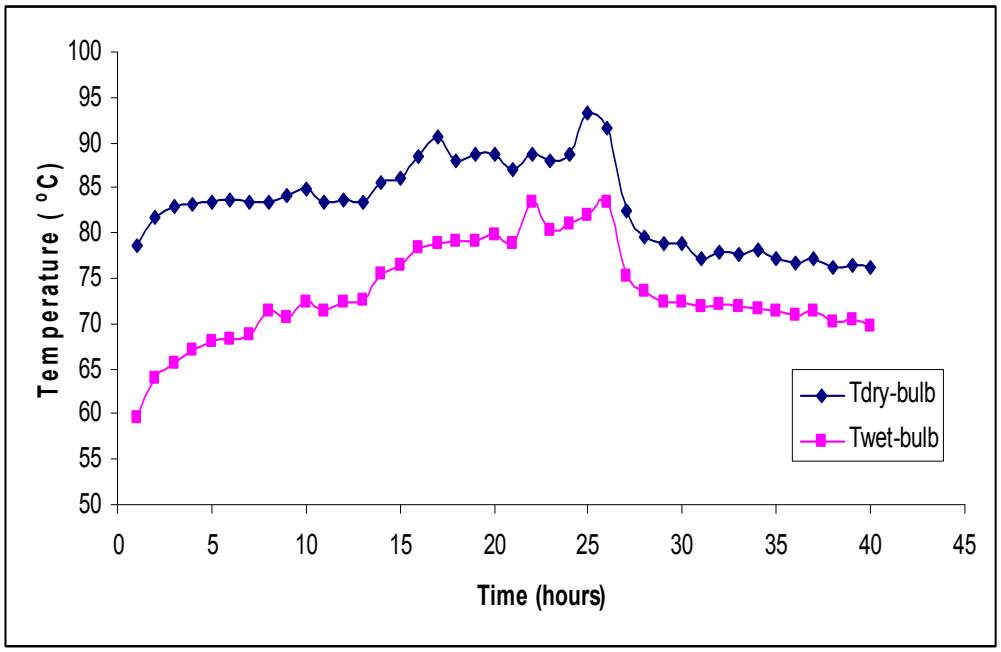


Figure 4.2 Wet-bulb and dry-bulb temperature profile for the kiln drying experiment using the Fogarty Kiln Dryer (trial I).

4.2 Final Moisture Content

The goal of the drying was to obtain final moisture content (FMC), between 8 to 10%. The FMC was influenced by the drying time, initial moisture content, and the type of wood that was being dried. In order to reduce the effect of the initial moisture content and the type of wood, radiata pine sapwood with initial moisture content 110-160% was used. Therefore, the variable that influenced the FMC was mainly drying time.

The first trial was run for 40 hours and the average FMC was 5.98 % indicating excessive drying. In order to achieve the desired moisture content, the time for the next trials was adjusted. The second trial was run for 30 hours and the average final moisture content was 7.82 %. In third trial, the average final moisture content was 7.38% after approximately 32 hours. In the fourth trial, the final moisture content was 8.06% after approximately 28 hours. Based on these trials, the maximum drying run time was 28 hours for this particular system.

4.3 Condensate from the Drying Process

This procedure was done to determine the condensate production rate as well as to determine the total amount produced during the drying process. The condensate samples were obtained from four trials.

4.3.1 Condensate Collection

During the drying process, the condensate formed in the condensation chamber was collected every an hour initially and then every 2 hours. The volume of condensate acquired from the experiment and its profile are shown in Table 4.1 to 4.4 and Figure 4.3. The analyses which were conducted on the samples were TOC, COD, BOD, and GC to determine the organic contaminants in the samples.

Table 4.1 Condensate volume measured through the drying process from trial I

Trial I			
Volume Collected (ml)	Total Volume Collected (ml)	time (min)	flow rate (ml/min)
0	0	0	0
365	365	60	6.08
880	1245	120	14.67
1324	2569	185	20.37
1053	3622	245	17.55
1058	4680	300	19.24
1040	5720	360	17.33
960	6680	420	16.00
970	7650	480	16.17
4554	12204	1005	8.67
369	12573	1080	4.92
426	12999	1215	3.16
240	13239	1290	3.20
208	13447	1365	2.77
120	13567	1455	1.33
103	13670	1575	0.86
42	13712	1815	0.18
0	13712	2385	0.00

Table 4.2 Condensate volume measured through the drying process from trial II

Trial II			
Volume Collected (ml)	Total Volume Collected (ml)	time (min)	flow rate (ml/min)
0	0	0	0
318	318	60	5.30
708	1026	120	11.80
1032	2058	190	14.74
882	2940	240	17.64
888	3828	300	14.80
878	4706	365	13.51
672	5378	420	12.22
781	6159	490	11.16
627	6786	550	10.45
548	7334	610	9.13
380	7714	670	6.33
2130	9844	1160	4.35
245	10089	1390	1.07
420	10509	1570	2.33
170	10679	1800	0.74

Table 4.3 Condensate volume measured through the drying process from trial III

Trial III			
Volume Collected (ml)	Total Volume Collected (ml)	time (min)	flow rate (ml/min)
0	0	0	0
370	370	60	6.17
720	1090	120	12.00
1040	2130	180	17.33
1040	3170	240	17.33
985	4155	300	16.42
765	4920	360	12.75
735	5655	420	12.25
685	6340	480	11.42
965	7305	600	8.04
3155	10460	1500	3.51
655	11115	1915	1.58

Table 4.4 Condensate volume measured through the drying process from trial IV

Trial IV			
Volume Collected (ml)	Total Volume Collected (ml)	time (min)	flow rate (ml/min)
0	0	0	0
535	535	60	8.92
770	1305	120	12.83
895	2200	180	14.92
910	3110	240	15.17
900	4010	300	15.00
850	4860	360	14.17
950	5810	430	13.57
740	6550	485	13.45
790	7340	545	13.17
665	8005	605	11.08
3390	11395	1410	4.21
465	11860	1610	2.33
180	12040	1680	2.57

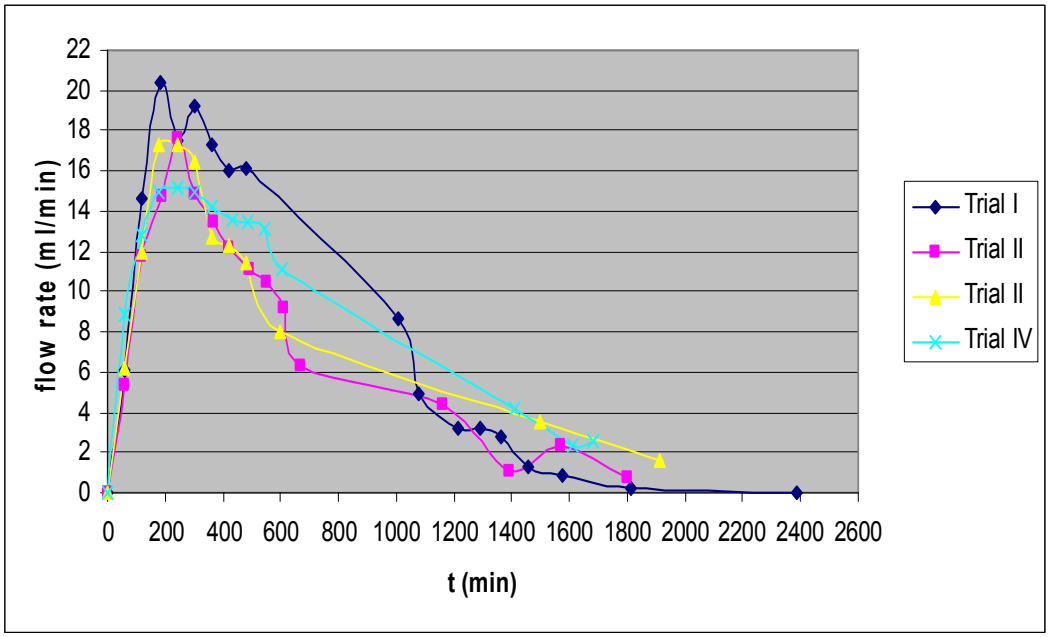


Figure 4.3 Condensate flow rate profile from four drying runs of *Pinus radiata* in the pilot-scale Fogarty kiln.

The results showed the condensate flow rate increased rapidly in the first 180 minutes and decreased slowly afterwards. In the beginning of the process, the

wood contained a large amount of water which was readily evaporated, resulting in a high flow rate of condensate (0 → 190 – 200 minutes). After this point, the surface water was depleted and the water, which resided deeper in the wood, came to the surface slowly replacing the water loss to evaporation. This region was marked by the decreased condensate flow rate. As the wood dried, the slower the water came to the surface, which was marked by a further decrease in condensate flow rate. This point is shown in the Figure 4.3 as the gradual drop in flow rate at 1000, 600, 420, and 545 minutes in Trial I – IV respectively.

4.3.2 Analyses on the Condensate Samples

From the previous studies done by Slovak (2003) and Davison (2005) on the kiln emission, seven organic contaminants were present in the gas phase: acetaldehyde, ethanol, methanol, formaldehyde, formic acid, acetic acid, and pinene. To confirm their presence in the liquid condensate, there were four analyses done on the condensate samples. They were TOC, COD, BOD and GC. TOC, COD and BOD analyses characterised the treatability of the condensate by biological methods. GC analysis was used to identify what contaminants were present in the condensate and their concentration.

4.3.2.1 TOC and COD Analysis

TOC and COD were done on some of the samples from Trial I and II to determine the TOC-COD ratio, with the Trial I samples used to learn how to operate the TOC and COD analyses instruments Trial II samples were used to determine the COD-TOC ratio as well as the of COD profile of the condensate (Table 4.5)

Table 4.5 TOC and COD result for Trial II.

Sample	Time passed after start up (min)	COD (mg/L)	TOC(mg/L)	COD/TOC
1	60	265	84.9	3.12
2	120	146	65.3	2.24
3	190	138	58.7	2.35
4	240	129	56.1	2.30
5	300	134	56.5	2.37
6	365	142	61.4	2.31
7	420	136	63.0	2.16
8	490	159	65.2	2.44
9	550	177	66.1	2.68
10	610	162	67.3	2.41
Average		158.8 $\pm$ 40.2	64.5 $\pm$ 8.23	2.44 $\pm$ 0.28

From Table 4.5, the COD values ranged between 129 and 177 mg/L, with the exception of the first sample which COD value was as high as 265 mg/L. The high COD value in the first sample can be explained as the hot air not only heats up and evaporates the water on the surface, but also strips the VOC readily available on it. This particular phenomenon was supported by the high water content in the wood initially, since it was a solvent for the water-soluble organic materials. The average COD value obtained from the samples was 158.8 mg/L.

The COD/TOC ratio varied between 2.1 to 2.7, except for the first sample which had a value of 3.12. The average of the COD/TOC ratio was 2.44. According to Mara and Horan (2003), for short chain fatty acid, the COD/TOC ratio increases as the chains get longer. Also, the COD/TOC ratio of municipal wastewater containing relatively simple organics is 3.0. However for combinations of various organics such as glucose, short chain fatty acids, glycerol and others, the ratio can be between 2.7 and 3.3. These results indicated that the overall organic contaminants present as a mixture in the samples were comprised of simple organic molecules.

The COD and TOC analysis only provided an indication of the wastewater strength and type. In order to better characterise of the wastewater, BOD and GC analyses were done on the samples that were collected from of trial II, III and IV. However, due to limited of instrument availability and time restrictions, the BOD analysis was only done on a few of the samples collected.

4.3.2.2 BOD Analysis

Initially, the BOD analysis used the procedures available in the manual of the Hach BODtrak instrument. However, the procedure was not clear about its ingredients and the treatment necessary for the sample, therefore the BOD standard analysis 5210D Proposed Respirometric Method was used. This standard method still suggested modifications according to the type of wastewater treated. These modifications were determined by comparing the results using the standard method and the modified method. The modifications were volume variation of seed solution, pH adjustment method, nutrient addition, and sample dilution.

Sample one from trial II was analysed based on the procedure provided by the Hach BODtrak manual book. There were four maximum BOD values that could be measured by the instrument: 35 mg/L, 160 mg/L, 350 mg/L and 700 mg/L. The range of 0 - 350 mg/L was used in this experiment since the COD results above showed that its value would not exceed 350 mg/L. There was no addition of nutrient buffer as suggested in the procedure since the seed solution was taken from the primary effluent of Christchurch Wastewater Treatment Plant which was assumed to contain sufficient nutrient for bacterial growth. However, in order to determine the impact of the nutrient addition, the seed solution volume was varied in the analysis. In this stage, the sample was not diluted

Table 4.6 The effect of seed volumes on the BOD analysis of sample 1 from Trial II.

Test no.	BOD_{actual} (mg/L)	COD (mg/L)	BOD/COD	BOD range and seed volume
1	46	265	17.4%	A
2	34	265	12.8%	B
3	43	265	16.2%	C

note: A = 0 - 35 mg/L, 15 ml of seed
B = 0 - 350 mg/L, 15 ml of seed
C = 0 - 700 mg/L, 20 ml of seed

The results indicated that the BOD range was 0 – 350 mg/L range. The difference between test 2 and 3 indicated that nutrient addition was necessary. Test 3 used more seed solution and gave a higher BOD value than Test 2. The low BOD/COD ratio indicated that the contamination in the condensate would only be partially treated by biological treatment. The results provided a standard method to measure BOD from the condensate sample.

The BOD analysis on the samples which came from trial III were done as per BOD standard analysis 5210D Proposed Respirometric Method (1995). In this experiment, the pH and phosphate buffer concentration was adjusted. According to the 5210D standard method, phosphate buffer, beside used as pH buffer, was also used by the microorganism as the source of phosphorus nutrient. Dilution of the sample was applied in order to obtain more accurate results. The application of the modification was applied on the sample number 1 taken from trial III and the result is as follow:

Table 4.7 BOD test result, modified BOD standard analysis (trial III sample 1).

test no.	BOD_a (mg/L)	COD (mg/L)	BOD/COD	Modification
Test 1	140	213	65.7%	A
Test 2	90	213	42.2%	B

note: A: 10 times diluted sample, pH was adjusted to around 7.0, and 0.06ml phosphate buffer (1.5 N) was added in 200 ml of the diluted sample
B: 10 times diluted sample, no pH adjustment, and 0.6ml phosphate buffer (1.5 N) was added in 200 ml of diluted sample

These results showed that the addition of phosphate increased the biodegradability of the organics in the condensate as the BOD/COD ratio increased significantly from 16.2 % to 65.7 %. The use of phosphate in the sample without initial pH adjustment gave a lower BOD. The use of phosphate buffer without pH adjustment (method B) was tried because the phosphate buffer was able to increase the pH to 7.0. However, the result is not as high as method A. The difference between the result for method A and method B maybe due to the variability of the test, but method A used for test 1 was used for the next BOD tests because it was suggested by the BOD standard analysis 5210D Proposed Respirometric Method. The dilution applied on the sample was also helped to improve the accuracy. Possibly due to dilution, reducing the level of toxicity (Anonymous 2008), e.g wood natural biocide.

The method suggested that after the analysis was done, a standard check be completed on the Hach BODtrak instrument with a standard glucose-glutamic acid solution, as proposed by the BOD standard analysis 5210D Proposed Respirometric Method (Eaton et al. 1995). The result of the analysis was 238 mg/L BOD, which was within the expected result (260 mg/L $\pm$ 30) indicating the instrument was working well.

BOD analysis was carried out for sample 1 and 2 from trial IV in order to confirm the previous results. Sample 1 had the highest value of COD, compared to the rest of the samples afterwards. Sample 2 was chosen because the COD value was representative of the majority samples in the trial. The dilution factor of test 1 and 2 were also varied (Table. 4.8).

Table 4.8 BOD test results for trial IV sample 1 and 2 using the Method A from table 4.7

Test no.	sample no.	BOD_a (mg/L)	COD (mg/L)	BOD/COD	Dilution factor
1	1	130	245	0.53	10
2	1	125	245	0.51	5
3	2	120	213.5	0.56	10

From the results, sample 1 which was analysed twice using a different dilution factor (DF), gave a similar BOD/COD ratio. This means that the dilution factor did not influence the result of the analysis.

The results also showed that the ratio of BOD/COD for sample 1 and 2 were similar, 0.53 and 0.56 respectively. This indicates that the kiln condensate was quite steady in general composition. It also shows that the wastewater was potentially biologically treatable, because the BOD/COD ratio was larger than 0.5 (Metcalf et al. 2003). According to Symons (1960), the BOD/COD should be more than 0.6 for the wastewater to be treated easily using the biological treatment; while the minimum required value for effective treatment is 0.4. The final version of the BOD analysis technique is detailed in Section 3.3.3.

4.3.2.3 Gas Chromatography Analysis

Based on the previous research by Slovak (2003) and Davison (2005), there were seven organic compound present in the gas stream leaving the drying chamber. They were acetaldehyde, ethanol, methanol, formaldehyde, formic acid, acetic

acid, and pinene. In the reports, these compounds were identified using a Selected Ion Flow Tube Mass Spectrophotometer (SIFT-MS) with a detection ability of billion (ppb) levels. It was expected that these components would appear as well in the condensate. The liquid condensate contaminants were analysed using gas chromatography (GC) with the flame ionization detection (Ch. 3.3.4). The initial results showed two dominant contaminants and 1-3 minor contaminants from samples collected at different times during drying Trial IV (Figures 4.4 – 4.8).

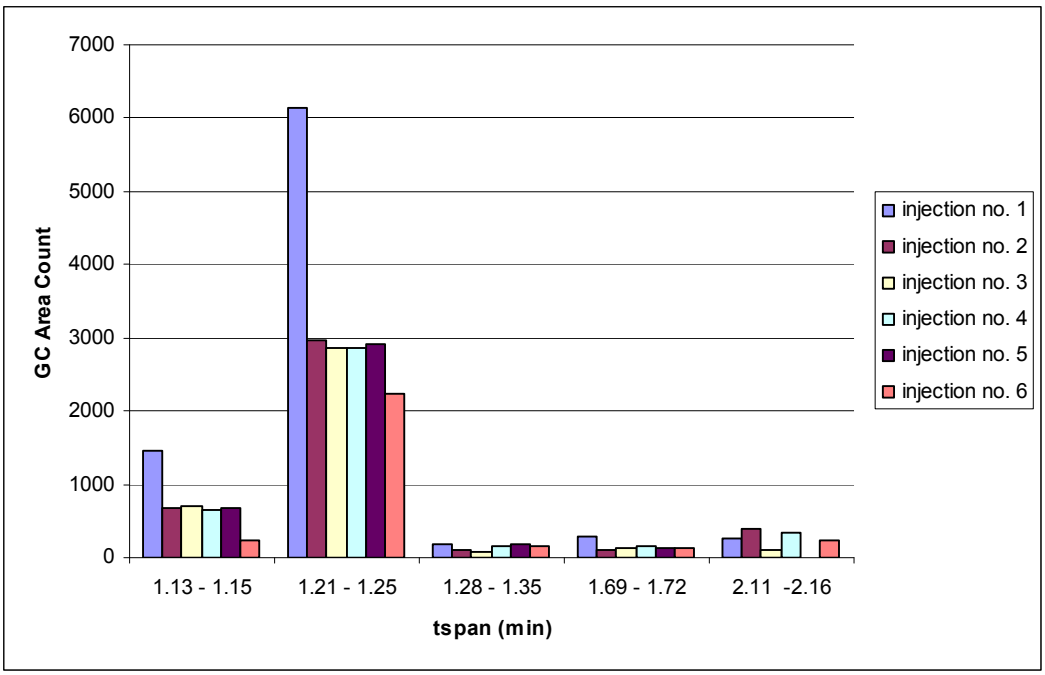


Figure 4.4 GC peak areas and retention times for unknown compounds. There were six injections for the condensate sample collected 1 hour after thestart of Trial IV.

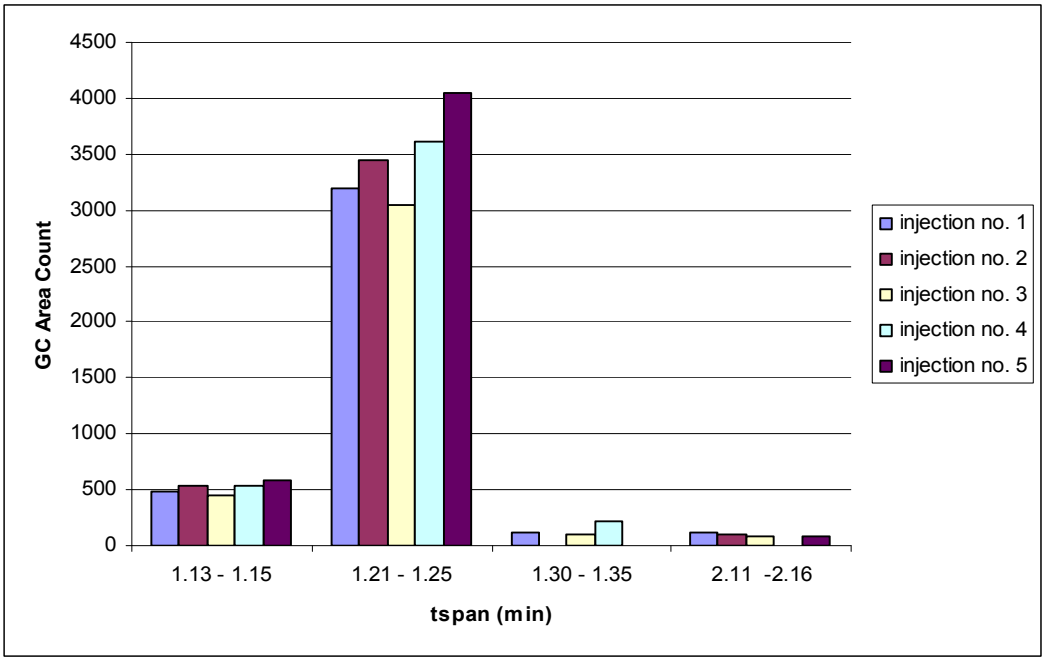


Figure 4.5 GC peak areas and retention times for unknown compounds. There were five injections for the condensate sample collected 2 hours after the start of Trial IV.

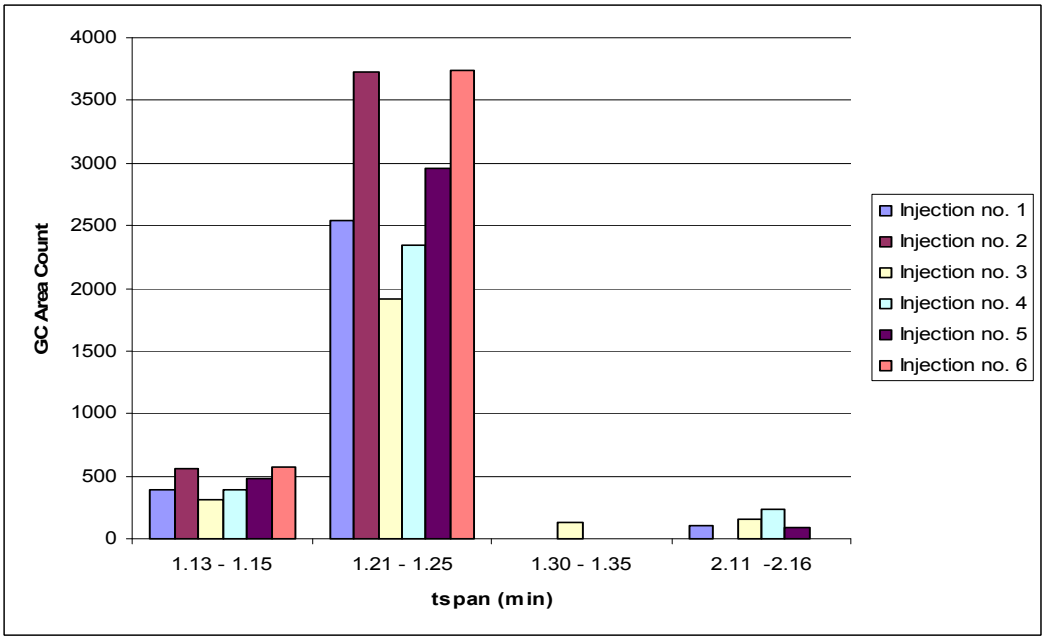


Figure 4.6 GC peak areas and retention times for unknown compounds. There were six injections for the condensate sample collected 3 hours after the start of Trial IV.

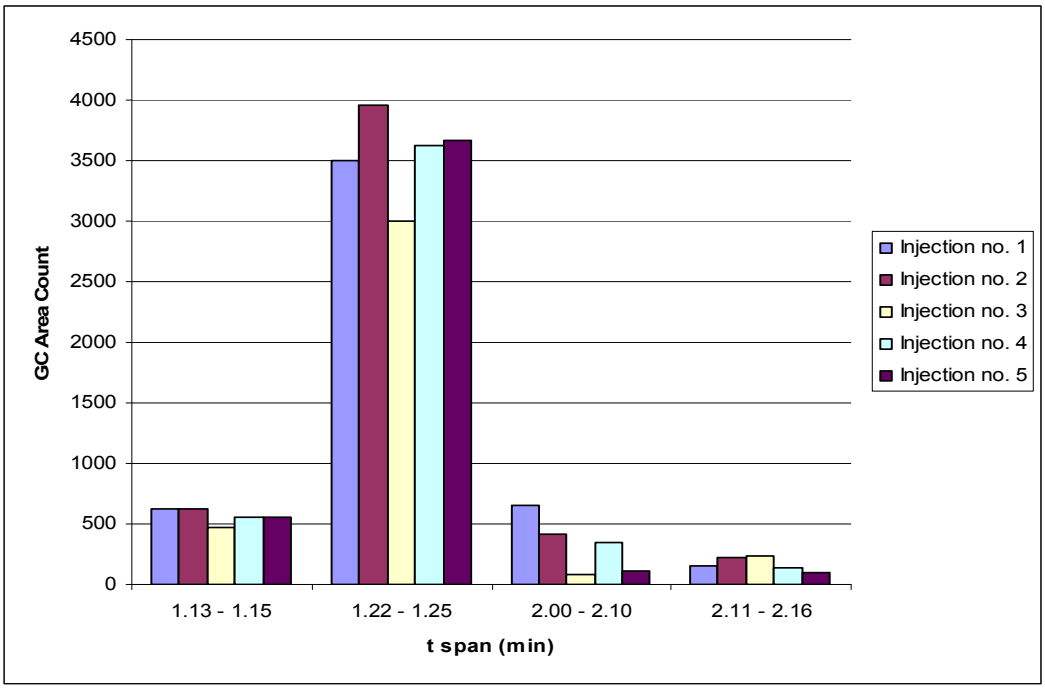


Figure 4.7 GC peak areas and retention times for unknown compounds. There were five injections for the condensate sample collected 4 hours after the start of Trial IV.

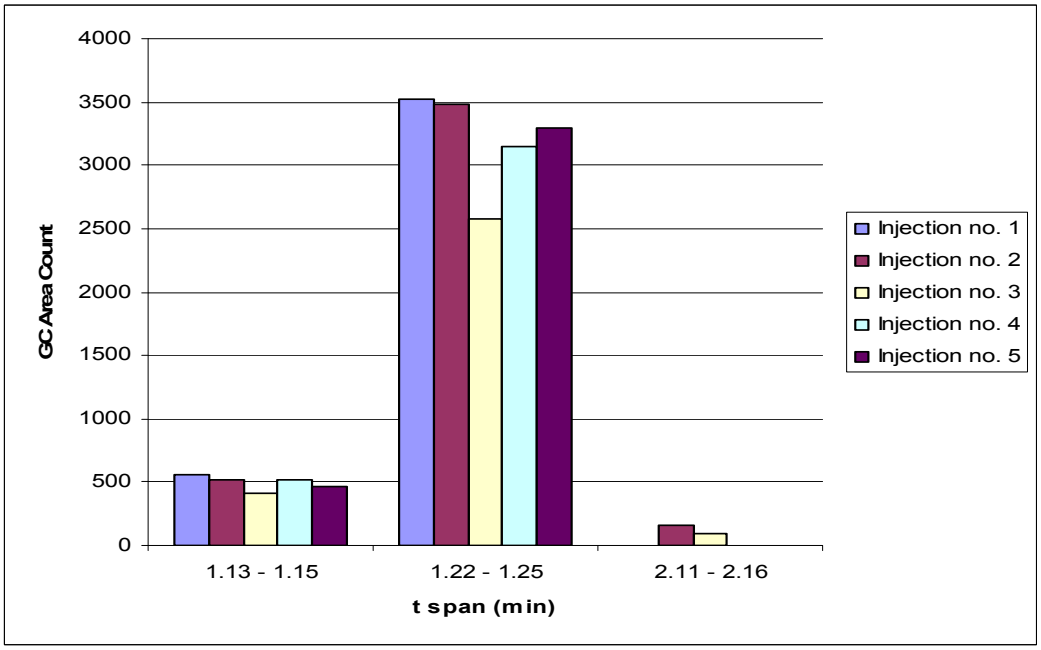


Figure 4.8 GC peak areas and retention times for unknown compounds. There were five injections for the condensate sample collected 5 hours after the start of Trial IV.

The results of the GC analysis of the first five samples of trial IV showed that the two dominant organic contaminants had retention times between 1.13 – 1.15 minutes and 1.22 – 1.25 minutes respectively. The other contaminants did not always appear and had relatively small peak areas compared to the ones mentioned above. Based on this result, the two peaks were considered to be the main contaminants in the condensate.

In order to identify the dominant peaks, the retention times were measured for the organic compounds mentioned in the previous research. The result showed that the dominant peaks were methanol (1.13 – 1.14 minutes) and ethanol (1.23 – 1.25 minutes) respectively. However, the other compounds that mentioned in the previous research were not detected by the GC. Based on the standard curves (Ch. 3.3.5), the average methanol concentration was 17.2 mg/L and ethanol concentration was 39.4 mg/L for the samples analysed in Figs. 4.4 – 4.8. The alcohol concentrations were used to estimate theoretical COD values and the results were compared to the actual COD analysis results (Table 4.9)

Table 4.9 The comparison between the measured COD analysis result and the theoretical COD calculation (Trial IV sample 1 – 5).

Sample No.	COD_{actual} mg/L	Ethanol O_2 requirement mg/L	Methanol O_2 requirement mg/L	$COD_{teoretical}$ mg/L	percentage %
1	245	83.5	34.2	117.7	48.1%
2	213.5	86.9	24.2	111.0	52.0%
3	201.5	71.8	21.1	92.9	46.1%
4	189.5	88.9	26.5	115.3	60.9%
5	186.5	80.3	23.0	103.3	55.4%

The result from these five condensate samples analysed from the GC showed that the COD theoretical, which only included the methanol and ethanol for COD source, was up to 60.9% of the actual. There were some possible explanations for the results. First, peak overlapping due to strong difference in abundance between

components: a large number of components with relatively lower mixing ratios may be completely masked by the enhanced baseline, so they are not visible in conventional chromatograms (Lewis et al. 2000). Second, the difference between the theoretical COD and actual COD might be due to involatility of some organic matter to be analysed directly by GC method (Anonymous 2009). Third, there were reactions between the organic compounds in the condensate which led to formation of less volatile organic compound. Last, the possibility of irreversible binding between the organic compound and the packing used by the GC instrument which immobilized the compound, causing to less organic compounds to be detected by the FID detector.

The detector used for the GC analysis was a flame ionization detector (FID). The GC/FID was very useful in determining the unknown volatile organic compounds in the condensate as well as their retention time because of its sensitivity to volatile organic compounds. The organic compounds were burnt when they passed through the detector. However, the drawback of GC is that the material has to be volatilized at 250^{o}C without decomposition. Some organics such as fatty acid and carbohydrates have to go through a derivation before they could be analysed using GC (Anonymous 2009).

The results from the GC showed that the most abundant volatile organic compounds were ethanol and followed by methanol. Other compounds were present in the condensate; however, they only appeared in few of the samples, while ethanol and methanol appeared in all of the analysed samples. It was not clear whether the other organic, such as formic and acetic acids, formaldehyde and acetaldehyde were in the samples. This was because the GC results did not show any peak when the standard solutions of these compounds were analysed their respective retention time. However, pinene was not in the condensate.

There were might be other organic compounds present in the condensate as well which were not detected by the GC, but contributed to the COD measurement.

The theoretical oxygen demand calculated from the GC analysis was similar to the BOD test value. This finding suggested the organics degraded during the BOD test were mainly ethanol and methanol. It concurred with the result obtained by Slovak (2003). She found that ethanol was the most dominant component in the emission, followed by methanol, formic acid, and acetaldehyde (Fig 4.9).

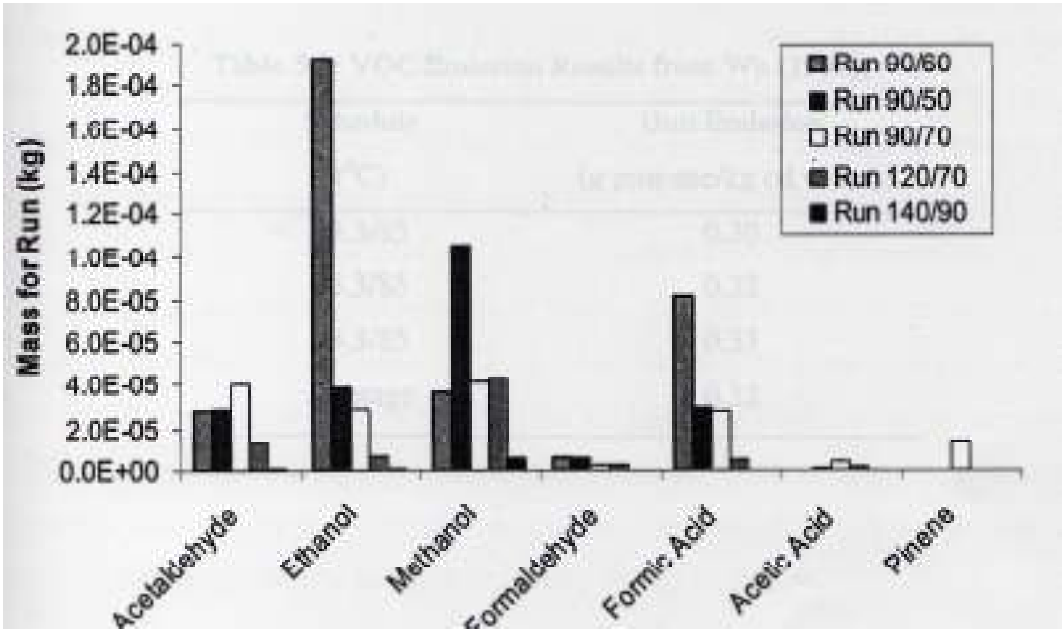


Figure 4.9 Total VOC emitted, analysed using SIFT-MS (Slovak 2003)

4.4 Main Treatment Preparation

The results from the previous analysis showed that ethanol and methanol were the dominant organic compounds present in the condensate. For testing purposes, an artificial wastewater containing those two compounds was created to replace the actual kiln condensate because of the volumes required. The pilot kiln size was inadequate to generate sufficient volumes to test the biological waste treatment options. Before the main experiment began, the reactor system was characterised.

4.4.1 Bed Void Fraction, Bed Residence Time (t_R) and Maximum Superficial Velocity (U_{max})

The bed void fraction was determined in the beginning in order to predict the residence time (Ch.3.2.1). The void fraction of the bed using the 2.8 – 4 mm diameter bark chips was 0.66 and for the 5.6 – 8 mm diameter bark chips was 0.59 (Table 4.10.)

Table 4.10 The void fraction of the bed using particular size of bark chips.

Bed no.	Barkchips size (mm)	ε_b
1	2.8 - 4	0.66
2	5.6 - 8	0.59

Bed 1 had a bigger void fraction than bed 2, indicating it would have longer residence time. This result was supported by the result obtained by Trejo-Aguilar (2005). He found that the residence time in a bed with larger void fraction would be longer than the one in smaller void fraction.

The residence time was an important characteristic of the bed. It gave the time spent by the liquid travelling through the bed. During this time, the exchange of material between the liquid and the biofilm happened. Generally, the longer the residence time, the better the quality of the water that came out from the treatment system. The residence time of the bed depended on the particle size and the inlet flow rate. In this project, there were two particle diameters of bed packing used: 2.8 – 4 mm and 5.6 – 8 mm. The result for the bed residence time determination versus flow rate is shown in Fig. 4.10. The residence time was determined by the amount of water collected in the outlet of the column divided by the inlet water flow rate (Ch. 3.2.1 part c).

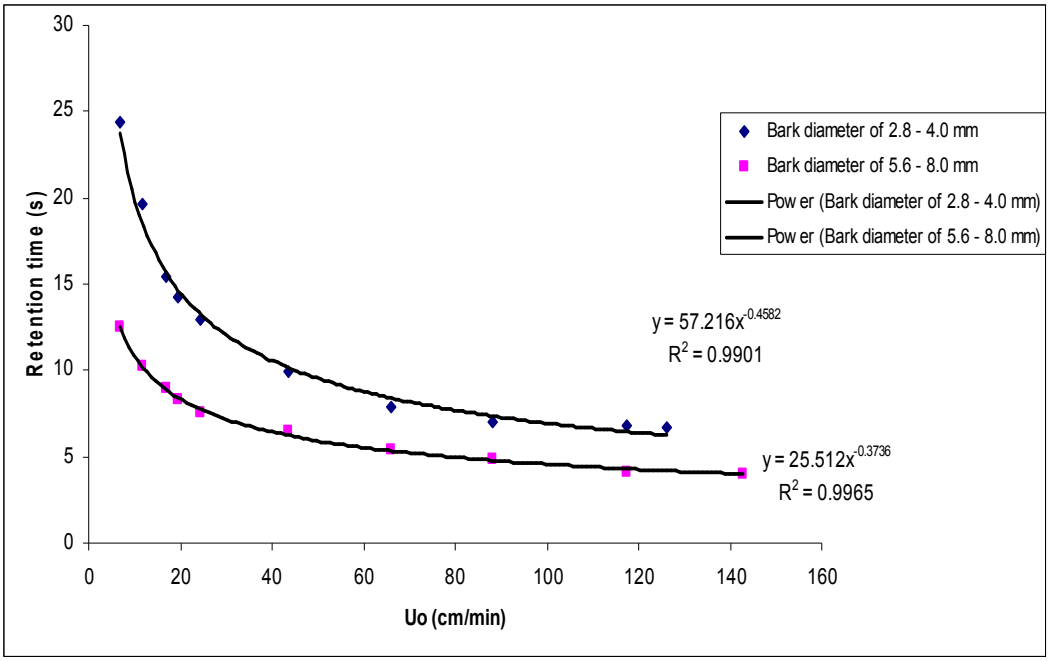


Figure 4.10 Residence time versus superficial velocity for particle sizes of 2.8 – 4 mm and 5.6 – 8 mm.

The results showed that the residence time for bed of smaller particles diameter was longer than the one with bigger diameter particles. This result concurred with the void fraction result, which indicated longer residence time for bed with larger void fraction.

The maximum superficial velocity without flooding was determined for both particle sizes. The bed that consisted of wood bark chips with an average diameter of 2.8 – 4 mm was flooded at 127.1 cm/min, while the bed using wood bark chips with an average diameter of 5.6 – 8 mm was not flooded at the pump maximum capacity of 393.9 cm/min.

4.4.2 Bed-column Organic Absorbance Capability

The acrylic column wall material was tested for absorption of the organic contaminant in the artificial wastewater. In this experiment, the bed material used

was glass beads. Sodium hydrazine was added at 0.01 mg/L to the artificial wastewater in order to prevent contaminant loss from microbiological activity.

The result showed that, initially, there was a reduction of contaminant concentration between the inlet and the outlet of the column. Since the microbiological activity was prevented by hydrazine addition, the reduction was due to the absorption of the column. However, the column absorption capacity was limited and diminished after approximately 1500 minutes, which represented around 140 bed volumes (Fig 4.11).

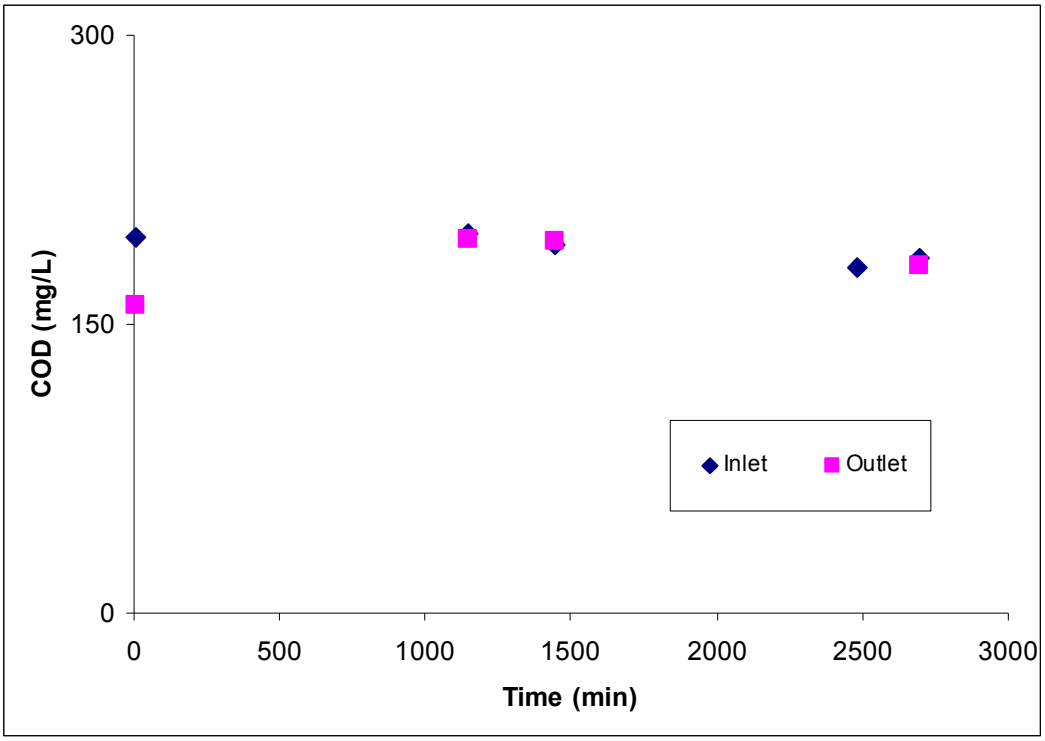


Figure 4.11 COD profile for the inlet and the outlet of a column filled with glass beads run with artificial wastewater with a flow rate of 2.8 ml/min.

4.4.3 Contribution of Wood Bark Chips Contaminant to the Wastewater Strength

This control test was done because fresh wood bark chips potentially contained extractable organic matter which might be released during the experiment. The water was run through the column and samples were taken from both the inlet and outlet. The COD test was done on those control samples and the difference indicating the organic released to the water.

The result demonstrated that there was no continuous contribution from the bark chips to the wastewater strength. There was a significant amount of extractable (103 mg/L) in the beginning of the control test (Fig 4.12). However the increased COD did not last long. The amount of extractable decreased in the next 110 minutes to a value of 19.5 mg/L of COD. After 230 minutes or approximately 22 bed volumes, there was almost no organic compound released from the bark into the water.

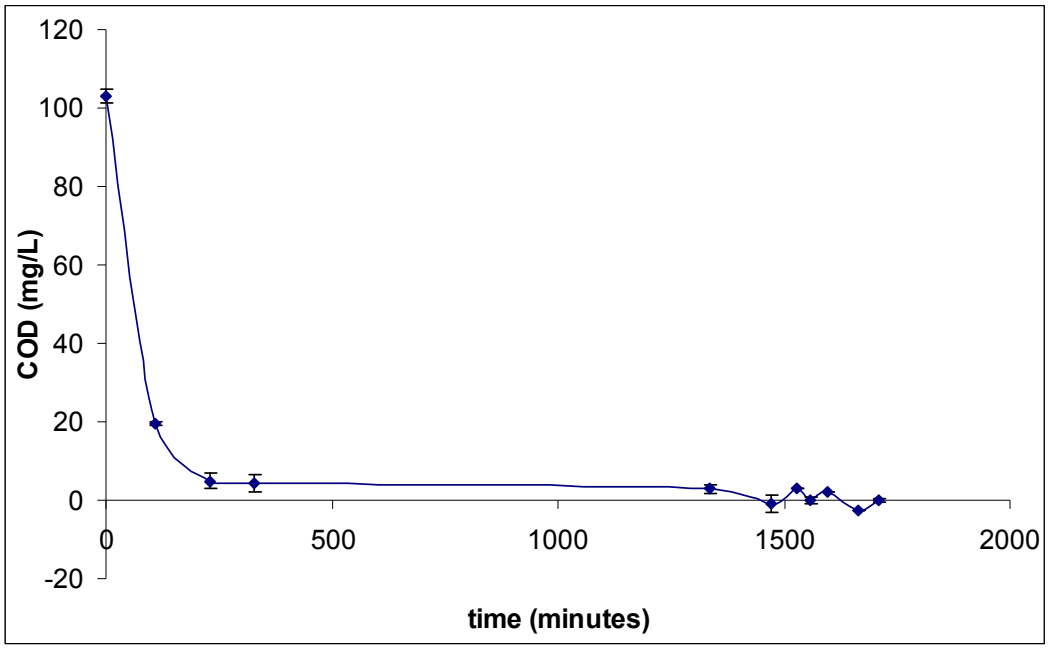


Figure 4.12 Contaminant release profile of radiata pine bark chips used as trickling filter media at an inlet flow rate of 2.8 ml/min.

4.5 Treatment of Condensate by Tricking Filter Technology

The experiment was done by using two different sizes of bark chips as support media: 2.8 – 4 mm and 5.6 – 8 mm. The base concentration was varied between 170 and 2720 mg/L and the flow rate was varied between 0.7 and 8.5 cm/min (Table 4.11).

Table 4.11 Trickle bed experiments varying in particle size, concentration and flow rate.

Bark Chip Size (mm)	COD Concentration (mg/L)	Flow rate (cm/min)
2.8 - 4.0	170	2.8
5.6 - 8.0	170	2.8
5.6 - 8.0	340	2.8
5.6 - 8.0	680	2.8
5.6 - 8.0	1360	2.8
5.6 - 8.0	2720	2.8
5.6 - 8.0	170	0.7
5.6 - 8.0	170	1.4
5.6 - 8.0	170	4.2
5.6 - 8.0	170	5.7
5.6 - 8.0	170	71
5.6 - 8.0	170	8.5

The commercial trickling filter processes usually recycle some of the effluent and mix it with the fresh feed in order to reduce the strength of the feed (Metcalf et al. 2003). It also has a schedule of nutrient addition in order to maintain the activity of the microorganisms, which are responsible for the removal of organic contaminants. In addition, these processes are often followed by a sedimentation system in order to settle out the solid particles that come out together with the effluent, before it is discharged. However, in these experiments, there was no recycle of the effluent and there was no periodic nutrient addition to the system.

4.5.1 Treatment of Condensate by Using 2.8 – 4 mm diameter Bark chips as Support Media

The first experiment was done by using bark chips with an average diameter of 2.8 – 4 mm diameter as the support media for bacterial growth. The main reason for using the bark chips with this diameter was because of the size of the column diameter used. In this experiment, the acrylic column used had a 3 cm inside diameter and 35 cm height. The practice in the literature was a column diameter – particle size ratio, D_C:D_P of 10:1 to 2:1 (Jones Saliling et al. 2007), (Arulneyam et al. 2004), (Sempere et al. 2008), (Dermou et al. 2005). The other reason for choosing this diameters range was the available surface area for the attached microorganisms. However with smaller particles, the possibility of clogging, channelling and other problems associated with trickling filter operation was higher as well.

The column was fed with an artificial wastewater, consisting of methanol (25 mg/L) and ethanol (65 mg/L) with a theoretical COD concentration of approximately 170 mg/L. The feed flow rate was 1.4 cm/min (10 ml/min) for 14 days and operated at higher flow rates. With the flow rate of 1.4 cm/min and 2.8 cm/min, the residence time of the wastewater was 49 seconds and 36 seconds respectively. The load per day was calculated based on the flow rate and the inlet COD concentration, since it varied from one analysis to the next and it had a tendency to decrease around 7 – 8 % per day.

The result of the treatment with the low flow rate (1.4 cm/min) showed that initially there was some removal of the contaminants in the wastewater (Fig.4.13). However, after the result at day 9.3, filtering was thought to be required prior to analysis, because biofilm was observed in the outlet sample (Fig 4.14). The results from samples taken at day 11.4 and 12.1 also indicated that the use of filtration was necessary. At day 9.3, the removal was -3.2 kg COD/m^3_{bed}•day because the biofilm increased the COD concentration in the outlet sample (Fig 4.15). The

filtration was applied for the first time on sample taken at day 12.3. At this flow rate, the maximum COD removal was 16.8%, achieved at day 14, with removal capacity of 1.74 kg COD/m^3_{bed}•day.

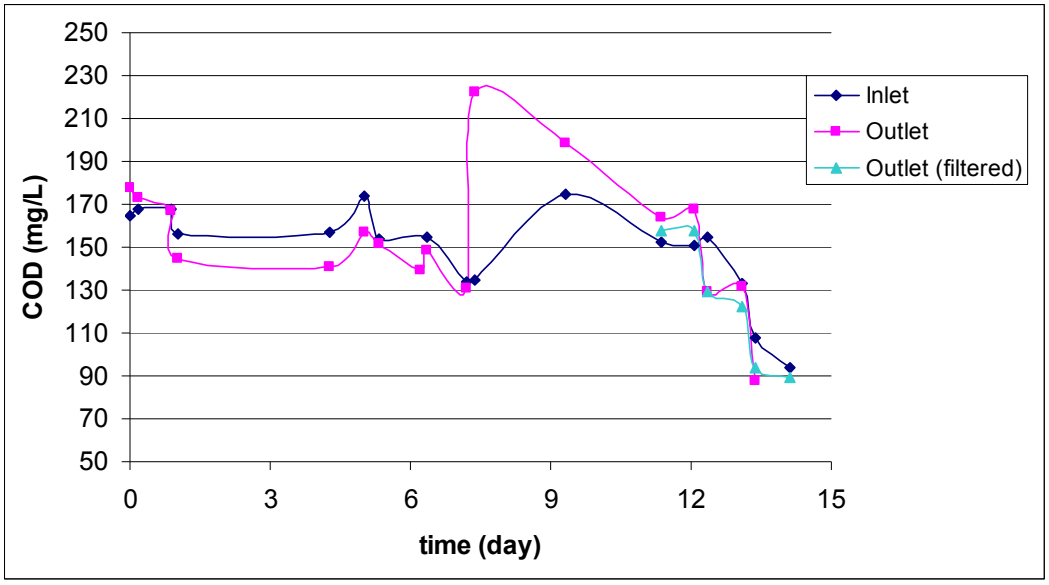


Figure 4.13 Performance profile of a trickling filter with a medium size of 2.8 – 4 mm and inlet flow rate of 1.4 cm/min from day 1 to 14.

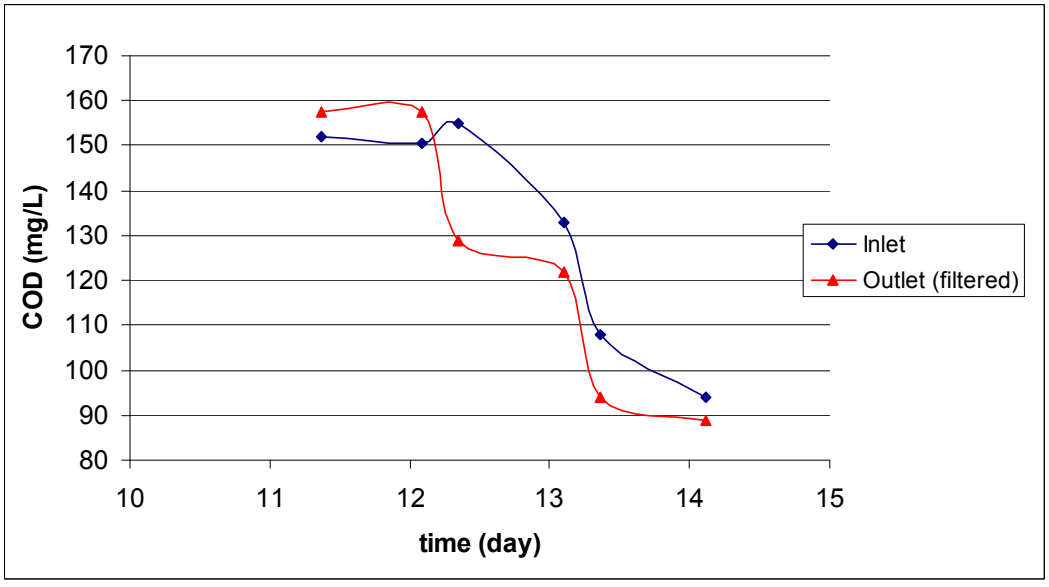


Figure 4.14 Performance profile of a trickling filter with a medium size of 2.8 – 4 mm and inlet flow rate of 1.4 cm/min from day 11 to 14.

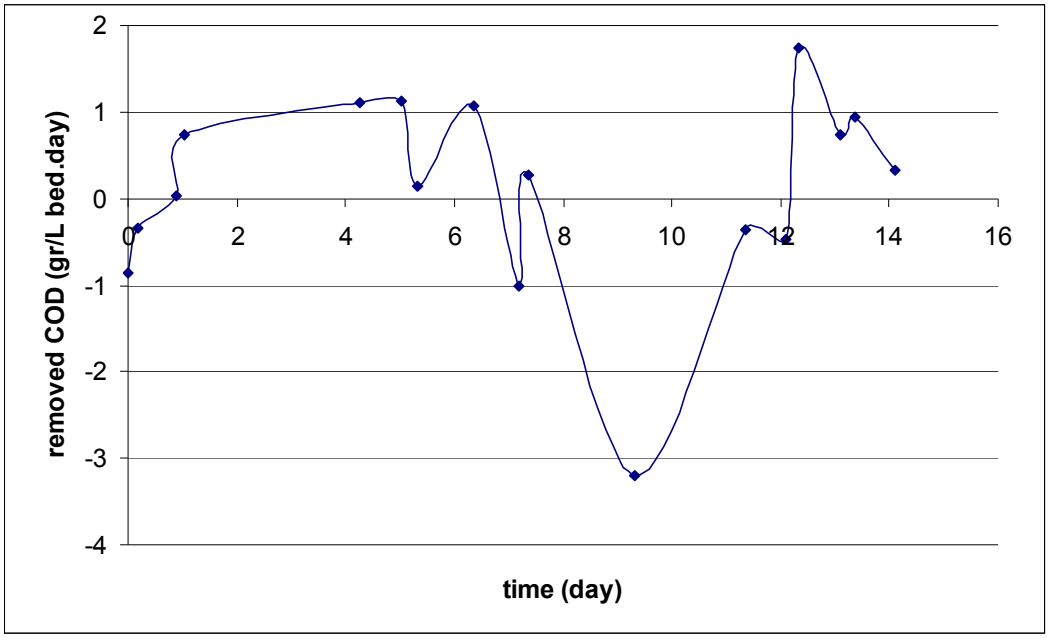


Figure 4.15 The removal capacity of a trickling filter with medium size of 2.8 – 4 mm and inlet flow rate of 1.4 cm/min from day 1 to 14.

After day 14, the flow rate was increased to 2.8 cm/min and held constant for 42 days (Fig. 4.16, 4.17). At this flow rate, the system removed up to 36.4 % of the feed COD but on some days the filtered outlet was still higher then the inlet, giving removal efficiency less than zero (Fig 4.18). The maximum removal was achieved right after the flow rate increase. However, the removal results varied greatly. It was also observed that the removal capability of the system was increasing before it suffered from clogging. The clogging was caused by biofilm accumulation. The clogging was removed by placing the bark chips into a beaker and washing them with tap water. The experiment was run until day 56 before it was stopped due to the bed clogging (day 25, 35, 47). During this period, the highest removal capacity was 8.34 kg COD/m^3_{bed}•day (day 14), achieved right after the flow rate change (Fig. 4.18). However, due to the clogging, the larger particles were tested in the column.

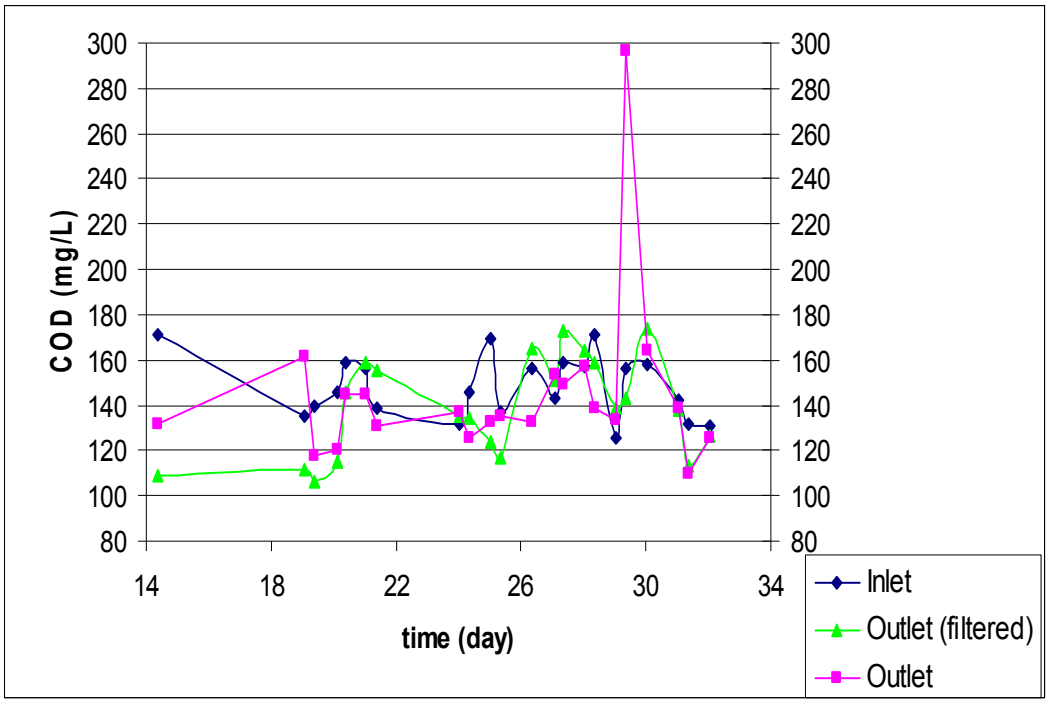


Figure 4.16 Performance of a trickling filter with a medium size of 2.8 – 4 mm diameter and inlet flow rate of 2.8 cm/min from day 14 to 30.

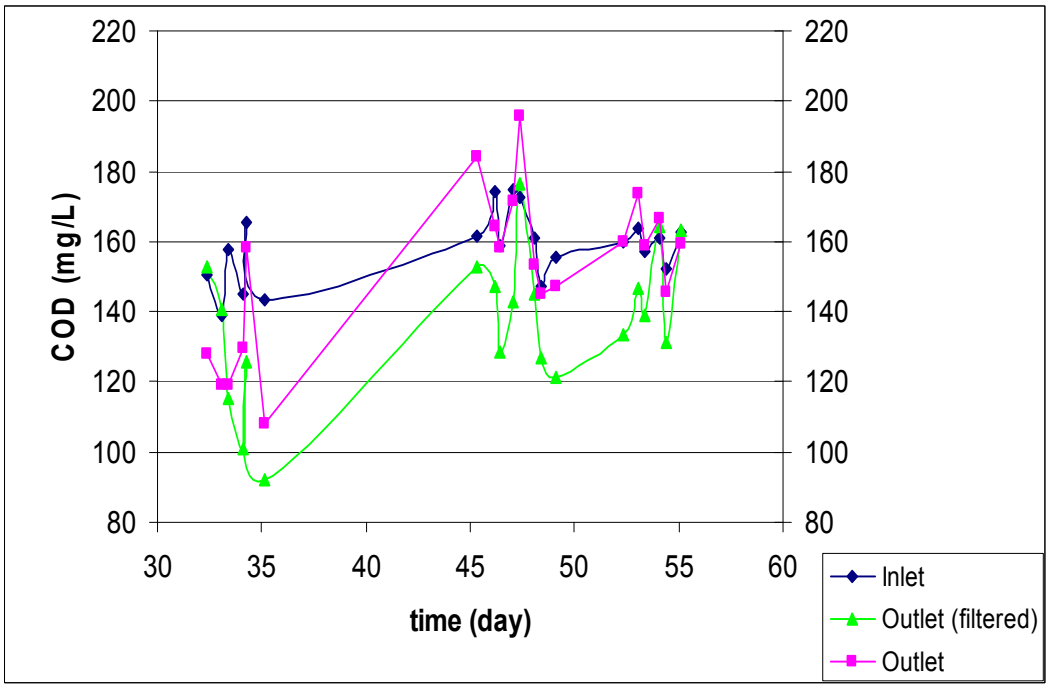


Figure 4.17 Performance of a trickling filter with a medium size of 2.8 – 4 mm diameter and inlet flow rate of 2.8 cm/min from day 31 to 56.

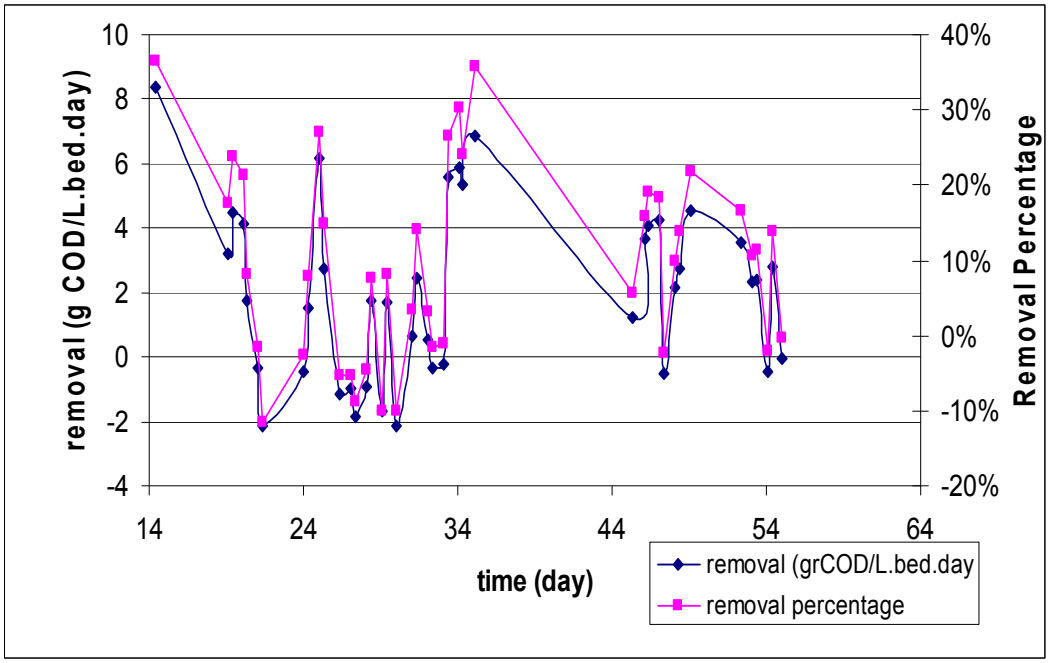


Figure 4.18 The removal rate and removal percentage of a trickling filter with 2.8 – 4 mm diameter bark chips medium.

4.5.2 Treatment of Condensate by Using 5.6 - 8 mm diameter Bark chips as Support Media

The column was repacked with larger bark chips (5.8 – 8 mm). Both the flow rate and wastewater concentration was varied to vary the load. Two identical columns were used. In the beginning, both were operated identically and afterwards the flow rate was changed in one and inlet concentration was changed in the other.

Using 5.6 – 8 mm bark chips with a flow rate of 2.8 cm/min and same inlet concentration of approximately 170 mg COD/L, the highest removal percentage was 28.1 % with removal rate of 5.97 kg COD/m^3_{bed}•day. This result was smaller than the one obtained from the previous experiment, however, the residence time was 17 seconds for flow rate of 2.8 cm/min, which was less than half of the residence time for the same flow rate with the smaller bark chips. It was also found that the problem of outlet COD being higher than the inlet was rarely

happened. It happened three times during the treatment. The higher outlet COD was observed to be happened before the bed was clogged. Since the individual void formed by the larger bark chip was bigger compared to the smaller bark chips, it was rarely clogged by the excess slime.

4.5.2.1 Effect of COD Load on Removal Rate and Efficiency

The loading was increased by increasing the concentration of the artificial wastewater. The loading rate was calculated based on the measured COD value obtained from the test, instead of the theoretical initial COD (TIC) value. The value of the measured COD was usually less than the TIC. There were some causes for this. First, volatile compounds were only oxidized to the extent with which they stayed dissolved in the liquid media (Eaton et al. 1995). Second, the heat generated from adding sulphuric acid during the COD analysis may have driven VOCs out of the solution (Wolff 1975).

The removal rate was a function of the inlet concentration, which also affected the loading rate (Fig. 4.19). The average removal rate increased as the average inlet COD concentration increased from 150.4 mg/L (19.1 kg COD/m^3_{bed}•day) to 668.1 mg/L (84.9 kg COD/m^3_{bed}•day), from an average of 3.8 kg COD/m^3_{bed}•day to 13.5 kg COD/m^3_{bed}•day. The removal rate started to decrease when the inlet concentration was increased further to 935.3 mg/L (119.0 kg COD/m^3_{bed}•day). At this inlet concentration, the average removal rate dropped from 13.5 kg COD/m^3_{bed}•day to 12.5 kg COD/m^3_{bed}•day. Increasing the inlet further only slightly decreased the removal rate to 11.6 kg COD/m^3_{bed}•day, when the inlet concentration was doubled to 1977.7 mg/L (251.7 kg COD/m^3_{bed}•day). However, the uncertainty increased, and according to a t-test, there was no difference in the removal rate above 668.1 mg/L. The increased removal rate up 668.1 mg/L was most likely due to the increased driving force/mass transfer provided by the higher concentration of COD. At higher concentration, the removal rate became constant implying a biofilm fully utilized by the organic contaminant.

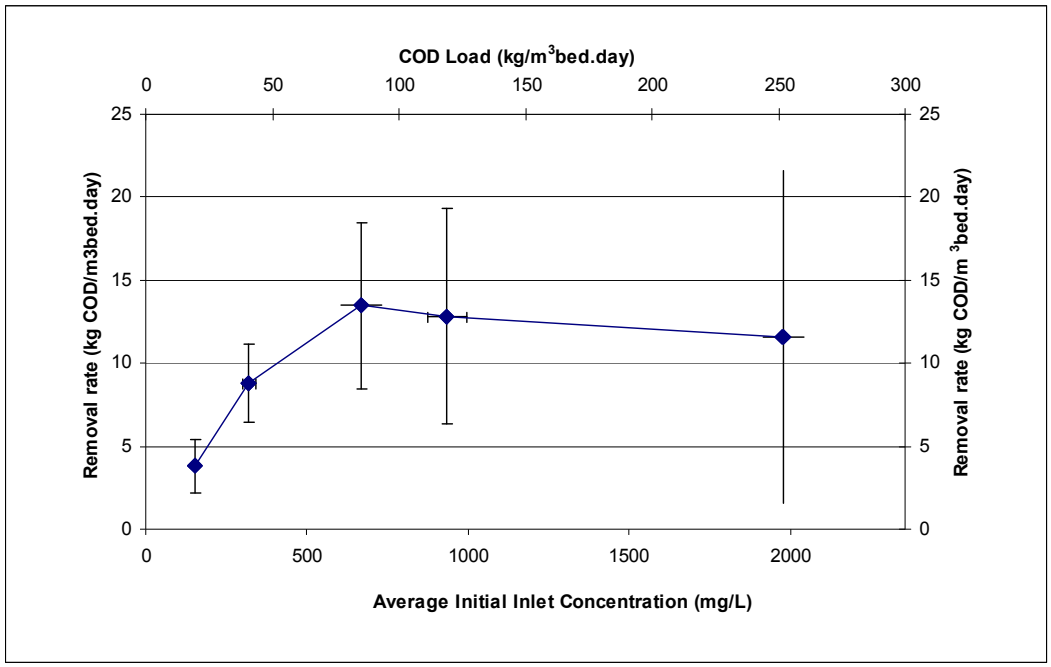


Figure 4.19 The effect of inlet COD concentration on the removal rate of the trickling filter with bark chips of a diameter range of 5.6 – 8 mm at flow rate of 2.8 cm/min. Each error bar is the standard deviation based on 13, 15, 31, 25, and 65 data points respectively.

The removal percentage increased when the inlet COD concentration was increased from an average of 150.4 mg/L (19.1 kg COD/m^3_{bed}•day) to 319.8 mg/L (40.7 kg COD/m^3_{bed}•day), with the removal percentage of 19.7 % and 21.7 % respectively (Fig 4.20). However, a t-test indicated that there was no significant difference. The further increase in inlet COD load resulted in a decrease of removal percentage, 15.9 %, 12.8 %, and 4.6 % at an inlet COD concentration of 668.1 mg/L (84.9 kg COD/m^3_{bed}•day), 935.3 mg/L (119.0 kg COD/m^3_{bed}•day), and 1977.7 mg/L (251.7 kg COD/m^3_{bed}•day) respectively.

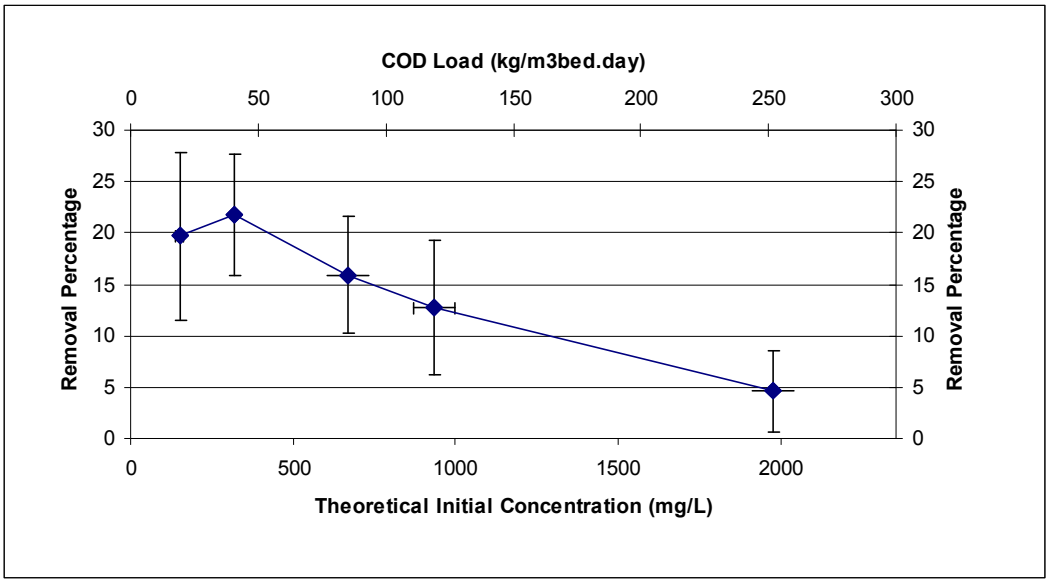


Figure 4.20 The effect of inlet COD concentration on the removal efficiency of the trickling filter at flow rate of 2.8 cm/min. Each error bar is standard deviation, made from 13, 15, 31, 25, and 65 data points respectively.

4.5.2.2 Effect of Bed Residence Time on Removal Rate and Efficiency

The removal rate was a function of the residence time (Fig 4.21). The residence time for a particular flow rate is shown in Table 4.12. The average removal rate increased as the inlet flow rate increased from 0.7 cm/min to 7.1 cm/min. Over this range, the average inlet COD load increased from 5.7 kg COD/m^3_{bed}•day to 53.3 kg COD/m^3_{bed}•day, while the removal rate increased proportionally from an average of 1 kg COD/m^3_{bed}•day to an average of 10 kg COD/m^3_{bed}•day respectively. The further increase of inlet flow rate up to 8.5 cm/min reduced the removal rate to 7.1 kg COD/m^3_{bed}•day but the uncertainty increased. From the results, the flow rate did not have a significant effect on the removal rate up to the inlet flow rate of 1.4 cm/min. This was most likely due to the incomplete bed wetting at low inlet flow rates caused by poor distribution at the inlet. At a flow rate of 0.7 cm/min, it was observed that there were dry surfaces in the bed. This resulted in the partial use of the available surface area. The increased flow rate led to increased wetted surface, thus increasing removal.

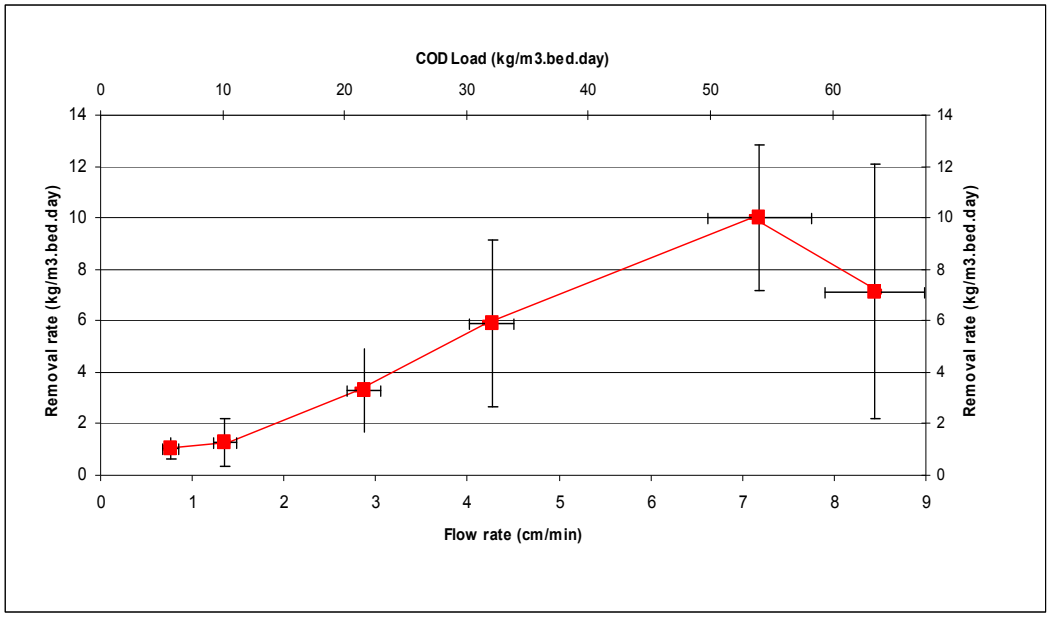


Figure 4.21 The effect of inlet flow rate on the removal rate of the trickling filter with and average inlet concentration of 158.1 mg/L COD, with 5.6 – 8 mm diameter bark chips. Each error bar is the standard deviation based on 14, 15, 15, 25, 24, and 31 data points respectively.

Table 4.12 Residence time based on the inlet flow rate achieved in the trickling filter with 5.6 – 8 mm diameter bark chips.

Inlet Flow Rate (cm/min)	Residence time (s)	Average COD load (kg COD/m^3bed•day)
0.7	29	5.7
1.4	22.4	10.2
2.8	17.3	21.7
4.2	14.9	32.1
7.1	12.3	53.3
8.5	11.5	63.4

The removal efficiency of the trickling filter varied with different flow rates, but the level of uncertainty was too great to tell whether there were significant changes (Fig 4.22). The t-test suggested that there were no significant difference between flow rate of 0.7 cm/min and 1.4 cm/min, 1.4 cm/min and 2.8 cm/min, 2.8 cm/min and 4.2 cm/min, and between 4.2 cm/min and 7.1 cm/min, However there

was significant drop in efficiency from flow rate of 7.1 cm/min to 8.5 cm/s, with the efficiency of 18.6 % and 11.2 % respectively.

The tendency of the data from 0.7 to 7.1 cm/min suggested that the active surface area increased as the flow rate increased. The increase of the active surface area should have increased the efficiency. However, as the flow rate increased, the residence time decreased, which had a negative effect on the efficiency. The maximum efficiency achieved in the experiment averaged 18.6 % at the flow rate of 7.1 cm/min.

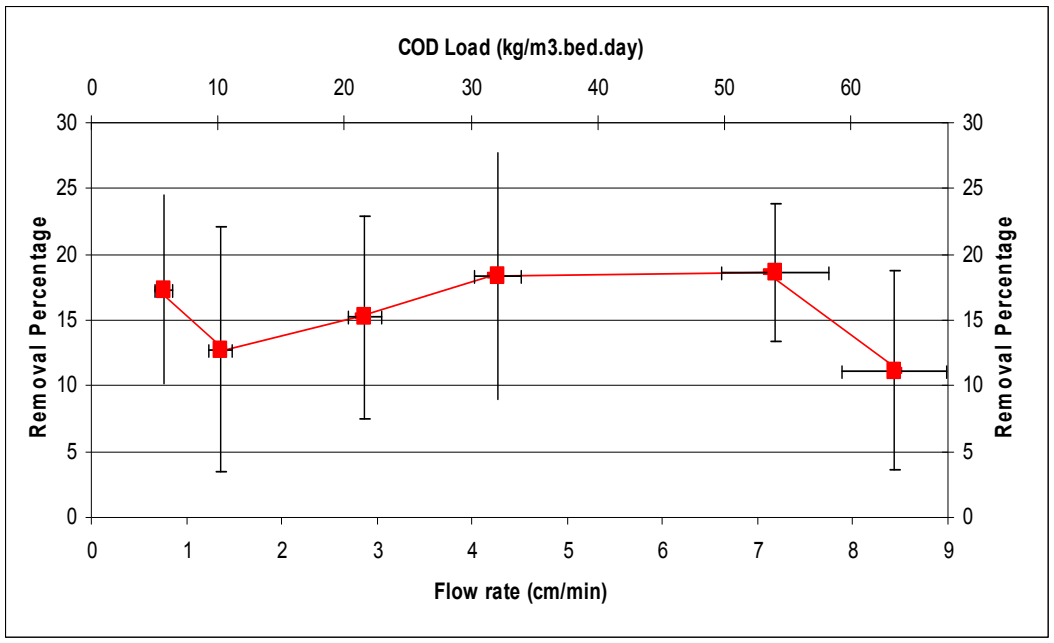


Figure 4.22 The effect of inlet flow rate on the removal efficiency of the trickling filter. Each error bar is the standard deviation based on 14, 15, 15, 25, 24, and 31 data points respectively.

The removal efficiency of the organic contaminants in the treatment process was not as good as expected. Ramirez et al.(2007) observed that at an inlet ethanol load of 1610 mg/L.h, a maximum elimination capacity of 970 mg/L.h was achieved, which approximately 60% of the inlet load. Meanwhile, in this research, with a total inlet load of 1909 mg/L.h, with the maximum removal capacity

observed was 573 mg/L. At this total load, the ethanol load was 1379 mg/L.h with ethanol removal capacity of 482 mg/L.h, which was approximately 35% of the inlet load.

A number of possible explanations for the low removal rate exist. The first possibility was the short residence time. The longest residence time achieved in the experiments was 29 seconds with an inlet flow rate of 5 ml/min. The second possibility was the influence of the contaminant type on treatment efficiency. According to Arulneyam et al. (2004), the presence of either ethanol or methanol in the mixture inhibited the biodegradation of the other. They found that the removal efficiencies for both methanol and ethanol were much less than for the individual substrate; even a low proportion of methanol (20%) in the mixture inhibited the degradation of readily-degradable ethanol (Fig 4.23). The inhibition was more obvious when the mixture contained 50% ethanol – 50% methanol was used (Fig 4.24). In this case, the ethanol removal was inhibited up to around 30 %, while the methanol removal dropped from 40% to 8%.

The fact that the contaminants presence in the wastewater contributed to the others' degradation process was not only found for methanol and ethanol. Jorio et al. (1998) found that the metabolism of toluene degradation was inhibited by the presence of xylene. Inhibition of methyl isobutyl ketone (MIBK) was hindered by the presence of methyl ethyl ketone (MEK) (Deshusses et al. 1993).

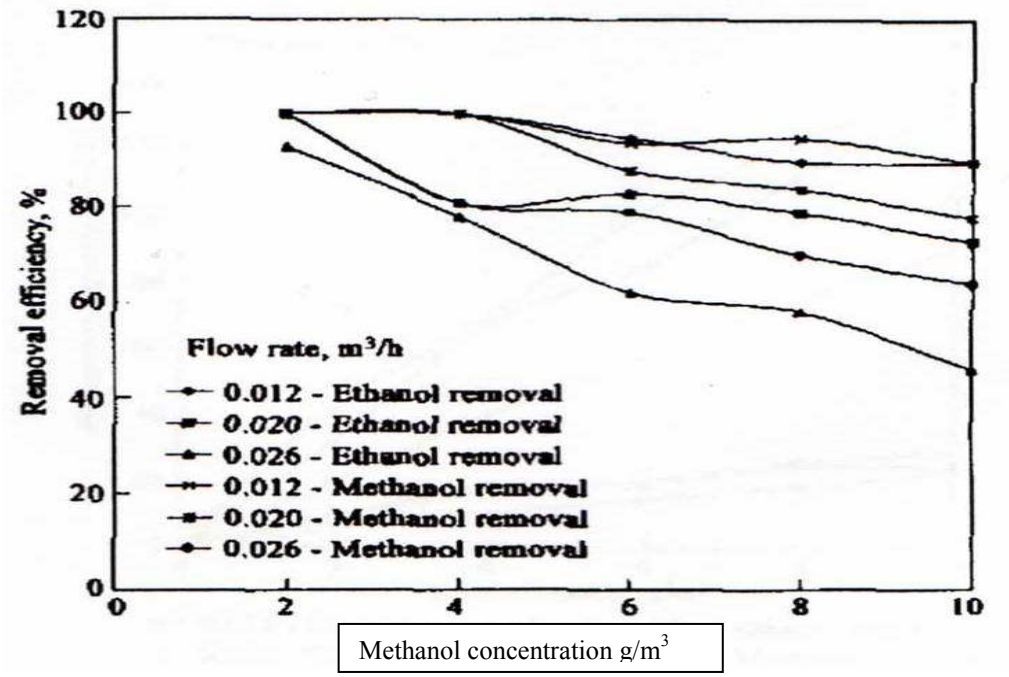


Figure 4.23 Ethanol and methanol degradation at different flow rates. The ethanol to methanol feed ratio was 5:1 on a weight basis (Arulneyam et al. 2004).

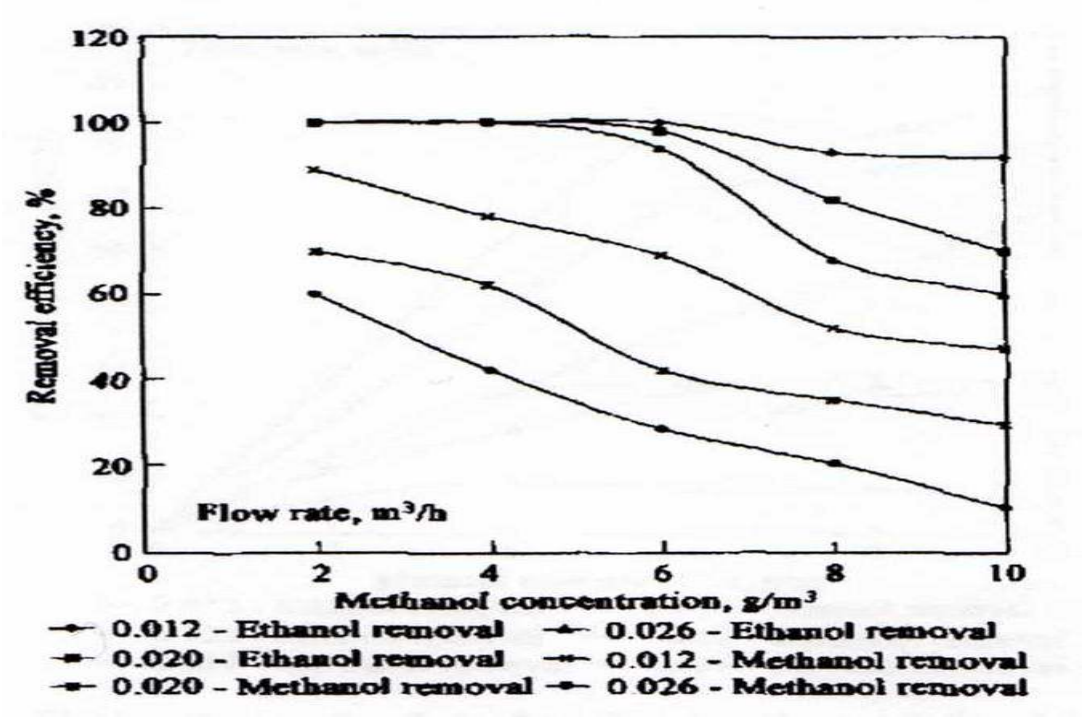


Figure 4.24 Ethanol and methanol degradation at different flow rates. The ethanol to methanol feed ratio was 1:1 on a weight basis (Arulneyam et al. 2004).

Arulneyam (2004) showed that there was removal preference towards the ethanol; while in this research, the gas chromatography results indicated that there was no preference between the removal of ethanol and methanol. The average result for both ethanol and methanol removal were 11.1% and 11.6 % respectively (Appendix B.4.4). It seemed that the concentration of the methanol also had influenced the removal preference. The concentration tested by Arulneyam (2004) was up to 10 mg/L; while in this research, the methanol concentration was up to 25 mg/L, which may lead to further decrease in the ethanol removal. This result was calculated from the GC result using the sample filtered by centrifugal filter. The ratio of methanol and ethanol in the feed was 5:13 mass/mass with a theoretical oxygen demand between 170 to 2720 mg/L.

4.6 The Effect of Increased Loading by Increasing the Initial Concentration and Feed Flow Rate on the Removal Rate.

In the experiments, the loading was increased in two ways: increasing the inlet concentration and increasing the flow rate. The result showed that the maximum removal rate of the experiment by increasing the concentration was higher compared to the maximum removal rate of the one by increasing the loading (Fig 4.25). It was also appeared that increased flow rate was only able to increase the removal rate up to 10 kg COD/m^3_{bed}•day at a load of 53.3 kg COD/m^3_{bed}•day, while the increased concentration was able to increase the removal rate up to 13.5 kg COD/m^3_{bed}•day at load of 84.9 kg COD/m^3_{bed}•day. A further increase in flow rate appeared to decrease the removal rate, but the uncertainty increased as well (Fig.4.21). It was suspected that a further increase in flow rate would not have much effect since it did not significantly reduce the residence time as occurred during low flow rates.

From the results, it was obvious that the removal rate was influenced by concentration, active surface area and residence time. However, it was not clear which one was the most dominant factor. The result of the experiment by

increasing flow rate, even though it increased the active surface area, the residence time was decreased in the process. In order to have significant removal (~90%), using the optimum flow rate obtained (7.1 cm/min), it was calculated that a column of 1.71 m length was needed (Appendix A.2), assuming there was no decreasing mass transfer from the feed to the biofilm due to the decreasing contaminant concentration. The column length of 1.71 m was calculated assuming a removal rate of 10 kg COD/m^3_{bed}•day at a loading rate of 53.3 kg COD/m^3_{bed}•day. In an actual kiln, producing around 400,000 m^3 of dry wood every year, the trickling filter plant would need to be at least 2.35 meters in diameter, with a bed height of 160 cm (Appendix A.3)

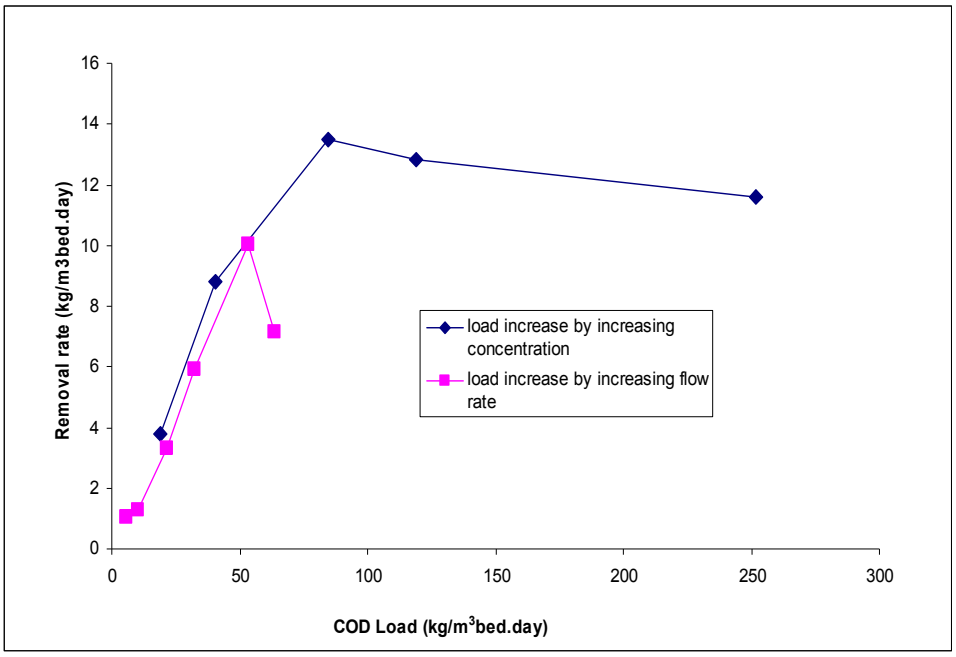


Figure 4. 25 The effect of increased load, by increasing concentration and flow rate, on the removal rate of trickling filter treatment.

4.7 Polymer Production

In the experiment, the samples that were analysed for their COD were also analysed using the GC to determine if the treatment showed a preference to methanol or ethanol removal. The samples were filtered using a 0.22 μm pore-size

membrane filter prior the COD and GC analysis. The data obtained from the GC was used to calculate the theoretical COD value and the result was compared to the value obtained from the COD analysis. It was observed that the value obtained from the COD analysis and COD calculation varied greatly, with the measured COD value generally higher than the COD value based on the methanol/ethanol concentration. The highest difference recorded between actual COD and calculated COD was 1128%. The difference between the two indicated that there was something present that did not show up in the GC analysis, but contributed to the COD measurement.

Initially, there were four possible causes for the difference: microorganisms, exopolysaccharide, humic substances resulted from the breakdown from the bark chips, and other soluble substances as the by-product or the microorganism activity that was not detected. However, microorganisms could not go through the 0.22 μm membrane filter. In addition, Kjehdahl nitrogen analysis conducted on an unfiltered sample of the treatment outlet showed little nitrogen indicating little biomass (Table 4.13). The analysis result on the sample was compared to the analysis result of the treatment column's biofilm taken from the bed using a spatula, and activated sludge biomass taken from local municipal wastewater treatment plant. The difference between the actual COD was believed due to the presence of soluble exopolysaccharides produced by the microorganisms in the condition of mal-nutrition. This substance was not detected in the GC, however, was detected by COD test.

Table 4.13 Kjeldahl nitrogen analysis on samples from of the trickling filter column biofilm, activated sludge and trickling filter outlet sample.

Sample	Nitrogen (%)
Column	17%
	15%
Sample	1%
	3%
AS	15%
	13%

The results showed that, based on the nitrogen content, the outlet stream contained a low fraction of microorganisms compared to the biofilm in the treatment column and activated sludge sample. This analysis also indicated that the fraction of microorganisms in the column's biofilm was similar to the activated sludge sample.

The results obtained from this analysis were further compared to the nitrogen content of some microorganisms. The result also shows that the nitrogen – solid ratio of the sample was much less than the suggested ratio for the microorganisms, indicating limited presence of microorganisms in the filterable fraction. The table of some of the microorganism nitrogen-solid ratio (shown as nitrogen percentage) was presented in table 4.14.

Table 4.14 The average percentage nitrogen for some microorganism (Shuler et al. 2002).

Compound	Mr	% N
biomass	24.5	9.1%
Bacteria	20.7	13.6%
Aerobacter aeroegenes	22.5	14.9%
Klebsiela aerogenes	23.7	13.5%
Yeast	23.5	8.3%
Candida utilis	25.5	11.0%

Further filtration using a centrifuge filter equipped with a membrane of 5000 molecular weight cut-off (MWCO) was applied to the samples. The result from using the centrifuge filter resulted in a difference of less than 35 % between the value from COD analysis and calculated COD from GC data. The result suggested that the difference was likely caused by the production of soluble exopolysaccharide which could go through the 0.22 μm membrane filter.

4.8 Ethanol and Methanol Removal Using Trickling Filter with Bark Chips as Support Medium.

The condensate produced from wood kiln drying mainly contained methanol and ethanol. The analysis by means of TOC, COD and BOD analysis showed that the condensate was able to be treated using biological means. Trickling filter technology was chosen because the condensate had a low contaminant concentration. In addition, this process has the advantage of ease of operation, low cost and low maintenance requirement. As a support medium for the trickling filter, bark chips were chosen because they are inexpensive and have a natural consortium of microorganisms.

The results from the experiments showed that the trickling filter system using bark chips as a support medium was able to treat wastewater containing methanol and ethanol. The result also showed there was no preference to the removal of either methanol or ethanol. From the % removal between the inlet and the outlet methanol and ethanol concentration, there seemed to be no preference. The removal percentage of methanol and ethanol based on the GC results were both around 10 -15%.

The variations used in this experiment were to increase the loading rate by increasing feed concentration and feed flow rate. Both variations were done in separate columns. In the experiment that carried out using bark chip with a diameter of 5.6 – 8 mm, it was found that increasing the loading by increasing the

flow rate and feed concentration resulted in increased removal rate. Higher feed concentration provided an increased driving force mass transfer, while higher flow rate provided a larger active surface area on the medium that increased removal rate. However, in this experiment, the advantage of high flow rate was offset by the reduction in residence time. In addition, there was a report showing that the presence of methanol and ethanol in a mixture inhibited each other removal.

Chapter 5 Conclusions

Several conclusions can be drawn from the study on the wood drying condensate organic contaminant removal by means of trickling filter process using radiata pine bark chips as a support medium. The dominant organic contaminant from the wood drying condensate samples as analysed by the GC were ethanol and methanol representing approximately 85 % of the total contaminant, with a concentration between 130 to 265 mg/L.

The overall experiment to determine whether bark chips could be used as a bed medium to remove the organic contaminant originating from a wood drying process was successful. Using artificial wastewater based on the dominant contaminants, the bark chips were able to remove the organic contaminant. In order to increase the removal rate of the treatment, the flow rate was increased. Increasing the flow rate provided more active surface area for mass transfer between the feed and the biofilm. Removal efficiency could be increased by using a longer column because a longer column would give a longer residence time at the same flow rate compared to shorter column.

Aside from the treatment system factors, there were additional explanations that may explain the low removal rate. First, there was no addition of nutrients during the experiment, since it was thought that the microorganisms were able to utilize the nutrients present in the support medium. Second, there was a possible interaction between the ethanol and methanol, causing inhibition of each other's degradation.

Based on the results, at removal rate of 10 kg COD/m^3_{bed}•day, an initial loading of 53.3 kg COD/m^3_{bed}•day, a flow rate of 7.1 cm/min, and a residence time of 12.3 seconds, it can be calculated roughly that the residence time needed to achieve complete removal was approximately 60 seconds. This could be achieved using a column with bed height of 171 cm, which is approximately five times the height

of the bed used in the experiment. For use with an actual kiln, which produces around 400,000 m^3 of dry wood every year, the size of the column will be at least 2.35 meters in diameter, with bed height of 160 cm.

Chapter 6 Recommendations

A number of recommendations for further study on the using bark chips as a support medium for a trickling filter:

- Addition of nutrients to the system to improve the removal capacity of the treatment system.
- Use of a recycle system in order to improve the effluent quality.
- Determine the influence of bark chips degradation on COD of the effluent.
- Microbial analysis in order to determine the type of bacteria present on the bark chips and their population. This analysis should be done to determine how the microorganisms react to the increasing load.
- Further analysis on the material which can only be filtered using centrifugal filter in this research and a better method to remove it.
- Use of longer column in order to achieve sufficient wetting while maintaining adequate residence time.
- Column inoculation with bacteria that can perform well in removing mixture of methanol and ethanol.

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Appendix A Calculations

A.1 COD Result Data and Calculation

Raw Data:

- COD inlet (C_{in}) = 174.5 mg COD/ml
- COD outlet (C_{out}) = 162 mg COD/ml
- Flow rate = 20 ml/min
- Bed Volume = 212.14 ml

Calculations:

- % removal = (174.5 – 162) / 174.5 x 100 %
  = 7.2 %
- Removal rate = [(174.5 – 162) / 1000] x [20 / 1000 x 24 x 60] / [212.14 / 1000]
  = 1.7 kg COD/m^3 bed•day
- Load = [20 x 1000 x 60 x 24] x [174.5 / 1000] / [212.14 / 1000]
  =23.7 kg COD/m^3 bed•day

A.2 Column Length Requirement

Data:

- Flow Rate (F) : 7.1 cm/min
- Residence time (t) : 12.3 s
- Removal Rate (R) : 10 kg/m^3•day
- Loading Rate (L) : 53,3 kg/m^3•day
- Bed height used (h) : 32 cm

Calculations:

- Residence time requirement (t_1) = (L / R) x t
  = (53.3 / 10) x 12.3
  = 65.6 s
- Bed height requirement (h_1) = (L / R) x h
  = (53.3 / 10) x 32
  = 170.6 cm
  = **1. 71 m**

A.3Actual Trickling Filter Calculation

Data:

- experiment TF: bed height (H) = 32 cm
  diameter (D) = 3 cm
  Flow rate (F) = 7.1 cm/min = 50 ml/min = 72 L/day
- removal rate (experiment) (R) = 10 kg COD/m^3_{bed}•day
- loading rate (experiment) (L) = 53.3 kg COD/m^3_{bed}•day
- Residence time at loading rate L (T) = 12.3 seconds

Assumptions:

- Wood data: oven dry density (ρ_{od}) = 450 kg/m^3
  Initial Moisture content (MC) = 150%
  Dry wood production (P) = 400,000 m^3/year
- Operation day in one year (t) = 360 days.
- Density of water (ρ_w) = 1000 kg/m^3

Calculations:

- Bed height to achieve complete removal (H_1) = (L / R) x H
  = (53.3 / 10) x 32

= **170. 56 cm**

- Mass of 1 m^3 of dry wood (DW) = 1 x ρ_{od}
  = 1 x 450
  = 450 kg
- Mass of water in the wood (M_w) = (MC x DW)
  = 150% x 450
  = 675 kg
- Volume of water in 1 m^3 of green wood (V_w) = Mw / ρ_w
  = 675 / 1000
  = 0.675 m^3
- Volume of water produce in 1 year (V_y) = Vw x P
  = 0.675 x 400,000
  = 270,000 m^3
- Volume water treated per day (V_d) = Vy / t
  = 270,000 / 360
  = 750 m^3/day = 750,000 L/day
- Volume of TF needed (V_a) = (Vd / F) x (π x 0.25 x D^2 x H_1)
  = (750,000 / 72) x (0.25π x $(1.5/10)^2$ x (170.56/10))
  = 3139.63 L = 3.14 m^3

- Diameter of the actual TF (D_a) $= [V/ (\pi \times 0.25 \times H_1)]^{0.5}$

  $= [3.14 / (\pi \times 0.25 \times 170.56/100)]^{0.5}$

  $=$ **2.34 m**

Appendix B Data and Intermediate Results

B.1 Column #2 COD Removal Efficiency and Removal Rate

B.1.1 Inlet Flow rate of 20 ml/min

days after start up	% removal	removal (kg COD/m^3 bed.day)	average	Flow rate (ml/min)	Load (kg COD/m^3 bed.day)	Standard deviation for removal
12.2	7.2	1.7	3.3	20	23.7	1.63
13.0	13.9	3.3		20	23.9	
13.2	18.8	4.1		20	22.1	
13.9	16.6	3.7		20	22.1	
14.2	-4.4	-0.9		20	19.9	
15.9	21.4	4.5		20	21.2	
17.2	10.8	2.1		20	20.0	
19.0	28.1	6.0		20	21.1	
19.2	15.5	3.3		20	21.7	
19.9	16.0	3.6		20	22.3	
20.2	10.9	2.3		20	21.3	
21.0	19.4	4.3		20	21.9	
21.2	18.2	3.6		20	20.6	
21.9	20.6	4.5		20	22.1	

B.1.2 Inlet Flow rate of 10 ml/min

days after start up	% removal	removal (kg COD/m^3 bed.day)	average	Flow rate (ml/min)	Load (kg COD/m^3 bed.day)	Standard deviation for removal
26.0	20.5	2.1	1.3	10	10.5	0.91
31.7	10.6	1.2		10	11.2	
32.7	9.9	1.0		10	9.6	
33.1	-6.7	-0.6		10	9.7	
33.7	16.3	1.7		10	10.2	
33.9	9.6	1.1		10	11.3	
36.6	6.2	0.6		10	9.8	
36.9	23.5	2.4		10	10.1	
37.6	11.7	1.2		10	10.1	
38.0	15.0	1.7		10	11.3	
38.6	10.6	1.2		10	11.2	
38.9	19.3	2.0		10	10.4	
40.6	28.7	2.9		10	9.9	
40.9	19.2	1.0		10	9.9	
43.6	-2.7	-0.1		10	7.6	

B.1.3 Inlet Flow rate of 5 ml/min

days after start up	% removal	removal (kg COD/m^3 bed.day)	average	Flow rate (ml/min)	Load (kg COD/m^3 bed.day)	Standard deviation for removal
43.9	14.0	1.0	1.0	5	6.8	0.43
44.6	15.3	1.1		5	7.0	
45.8	16.6	0.9		5	5.4	
47.6	3.9	0.2		5	4.8	
47.9	9.5	0.8		5	5.6	
51.6	19.4	0.9		5	5.8	
51.9	10.2	1.2		5	5.6	
53.6	19.9	1.5		5	6.3	
53.9	15.9	0.5		5	4.9	

54.6	17.7	0.8		5	5.5	
54.9	24.4	1.4		5	5.9	
57.7	14.3	0.7		5	5.1	
57.9	17.9	1.1		5	6.4	
59.6	31.7	1.9		5	6.0	
59.9	28.9	1.4		5	4.9	

B.1.4 Inlet Flow rate of 30 ml/min

days after start up	% removal	removal (kg COD/m^3 bed.day)	average	Flow rate (ml/min)	Load (kg COD/m^3 bed.day)	Standard deviation for removal
61.6	11.9	3.6	5.9	30	30.0	3.12
61.9	15.2	5.2		30	34.2	
64.6	10.0	3.1		30	30.6	
64.9	18.6	6.1		30	32.8	
66.6	22.5	7.9		30	35.3	
66.8	15.9	4.8		30	30.1	
67.6	11.1	3.6		30	32.0	
68.8	48.3	16.0		30	33.1	
69.6	19.5	6.6		30	33.9	
73.1	15.7	5.1		30	32.4	
76.6	20.3	5.8		30	28.6	
79.1	4.8	1.6		30	34.2	
79.6	12.0	4.1		30	34.0	
79.9	19.4	6.3		30	32.6	
81.6	8.2	2.7		30	33.6	
81.9	3.3	1.0		30	30.7	
83.6	32.4	11.3		30	34.9	
85.8	16.7	5.3		30	31.8	
86.7	14.7	4.6		30	31.3	

86.9	25.8	7.5		30	29.2	
88.6	29.9	9.6		30	32.0	
88.9	21.3	6.8		30	32.1	
90.6	17.4	5.6		30	32.3	
92.0	19.6	6.0		30	30.6	
92.6	24.6	7.3		30	29.8	

B.1.5 Inlet Flow rate of 50 ml/min

days after start up	% removal	removal (kg COD/m^3 bed.day)	average	Flow rate (ml/min)	Load (kg COD/m^3 bed.day)	Standard deviation for removal
95.1	32.9	17.0	10.0	50	51.6	2.85
95.6	26.4	14.3		50	54.0	
95.9	27.7	15.3		50	55.2	
97.6	15.0	8.1		50	54.1	
97.9	16.8	8.7		50	51.4	
98.9	21.3	11.4		50	53.5	
99.7	21.8	11.7		50	53.6	
102.0	18.0	8.1		50	45.3	
102.6	20.9	9.3		50	44.6	
102.9	24.5	13.9		50	56.8	
104.6	22.6	12.7		50	56.3	
105.9	16.8	10.4		50	61.6	
106.6	15.8	9.7		50	61.3	
106.8	14.2	7.8		50	55.0	
107.6	13.7	7.5		50	54.5	
110.0	17.5	9.8		50	56.2	
110.6	15.4	8.1		50	52.9	
110.9	16.2	8.3		50	51.2	
111.6	12.4	6.3		50	50.6	

113.0	17.1	10.2		50	59.4	
113.6	13.9	8.3		50	59.7	
113.8	14.0	7.1		50	50.9	
114.6	12.7	6.4		50	50.7	
116.8	17.7	9.8		50	39.6	

B.1.6 Inlet Flow rate of 60 ml/min

days after start up	% removal	removal (kg COD/m^3 bed.day)	average	Flow rate (ml/min)	Load (kg COD/m^3 bed.day)	Standard deviation for removal
117.6	16.7	11.2	7.1	60	66.6	4.96
117.8	6.6	4.1		60	61.9	
118.6	5.7	3.5		60	61.1	
118.8	9.9	6.1		60	61.5	
120.6	11.2	7.3		60	65.6	
120.8	2.8	1.8		60	64.8	
121.6	16.0	10.6		60	66.0	
125.1	10.4	5.5		60	52.9	
125.6	7.1	4.5		60	63.3	
125.8	19.8	13.4		60	68.0	
126.6	8.7	5.5		60	63.5	
126.9	11.4	7.7		60	67.8	
127.6	18.6	12.6		60	67.8	
127.2	11.1	7.1		60	63.9	
127.9	36.6	23.0		60	62.9	
137.3	7.0	3.7		60	52.3	
140.9	12.0	6.7		60	55.8	
141.2	4.0	2.4		60	61.5	
141.9	0.9	0.6		60	66.8	
144.4	2.8	1.8		60	65.4	

145.9	13.4	8.8		60	65.2	
146.2	11.0	7.3		60	66.4	
147.0	16.8	10.8		60	64.3	
147.2	2.0	1.2		60	62.1	
148.0	12.9	9.0		60	69.4	
151.3	25.0	15.3		60	61.1	
151.9	5.3	3.3		60	61.7	
152.2	10.4	6.5		60	62.5	
153.9	8.5	5.1		60	59.9	
154.2	1.8	1.2		60	66.6	
154.9	20.2	13.6		60	67.4	

B.1.7 Removal Efficiency Curve Data

flow rate (ml/min)	average loading (kg COD/m3 bed.day)	average removal efficiency (%)	Standard Deviation for loading	Standard Deviation for removal efficiency
5	5.7	17.3	0.67	7.17
10	10.2	12.8	0.94	9.32
20	21.7	15.2	1.16	7.67
30	32.1	18.4	1.81	9.39
50	53.3	18.6	5.13	5.23
60	63.4	11.2	4.09	7.63
20	20.5	14.0	2.37	7.24

B.1.8 Removal Rate Curve Data

flow rate (ml/min)	average loading (kg CODm3 bed.day)	average removal rate (%)	standard deviation for loading	standard deviation for removal rate
5	5.7	1.04	0.67	0.43

10	10.2	1.28	0.94	0.91
20	21.7	3.30	1.16	1.63
30	32.1	5.90	1.81	3.12
50	53.3	10.01	5.13	2.85
60	63.4	7.14	4.09	4.96
20	20.5	2.68	2.37	1.50

B.2 Column #3 COD Removal Efficiency and Removal Rate

B.2.1 1 x Inlet Concentration

days after start up	% removal	removal (kg COD/m^3 bed.day)	average	flow rate (ml/min)	load (kg COD/m3 bed.day)	standard deviation for removal
0.0		0.00		0	0.0	
0.7	26.8	5.79	3.79	20	21.6	1.60
1.7	16.9	3.12		20	18.5	
2.2	31.3	5.73		20	18.3	
2.7	29.4	5.73		20	19.5	
3.0	11.6	2.23		20	19.3	
5.6	26.9	5.03		20	18.7	
5.9	14.0	2.61		20	18.6	
6.6	27.3	5.09		20	18.6	
7.0	13.7	2.86		20	20.9	
7.6	19.0	3.95		20	20.8	
8.23	12.2	2.35		20	19.3	
8.9	21.8	4.01		20	18.4	
9.1	5.1	0.83		20	16.4	

B.2.2 2 x Inlet Concentration

days after start up	% removal	removal (kg COD/m^3 bed.day)	average	flow rate (ml/min)	load (kg COD/m3 bed.day)	standard deviation for removal
37.1	20.6	8.3	8.82	20	40.4	2.34
37.8	26.4	10.4		20	39.6	
41.3	13.7	5.5		20	40.3	
44.8	24.0	10.6		20	44.0	
47.3	8.6	3.8		20	44.5	
47.8	18.1	7.8		20	43.2	
48.1	23.4	9.9		20	42.1	
49.8	26.5	11.3		20	42.4	
50.1	23.3	9.8		20	42.1	
51.8	27.5	11.3		20	41.2	
54.0	19.2	7.6		20	39.8	
54.9	30.7	12.4		20	40.4	
55.1	24.0	8.9		20	37.2	
56.8	18.1	6.7		20	37.2	
57.1	22.0	7.9		20	35.9	

B.2.3 4 x Inlet Concentration

days after start up	% removal	removal (kg COD/m^3 bed.day)	average	flow rate (ml/min)	load (kg COD/m3 bed.day)	standard deviation for removal
57.3	25.3	21.1	13.5	20	83.2	5.02
57.6	26.2	21.5		20	82.2	
60.1	28.5	24.5		20	85.9	
60.6	20.9	17.9		20	85.7	
60.9	22.5	19.2		20	85.3	
62.6	24.7	20.5		20	83.0	
62.9	20.6	17.1		20	83.0	

63.9	11.3	9.5		20	84.6	
64.6	13.4	11.4		20	84.8	
67.0	14.8	12.0		20	81.4	
67.6	10.2	8.3		20	81.3	
67.8	26.0	22.7		20	87.2	
69.6	10.6	9.0		20	84.3	
70.8	12.2	10.1		20	83.2	
71.6	10.7	8.4		20	78.8	
71.8	12.3	11.1		20	89.9	
72.6	10.5	9.2		20	88.1	
75.0	12.0	10.4		20	81.4	
75.5	10.2	9.0		20	81.3	
75.8	12.2	10.9		20	87.2	
76.5	12.0	10.5		20	84.3	
77.9	12.4	10.6		20	83.2	
78.7	15.7	12.2		20	78.8	
79.6	13.2	10.2		20	89.9	
81.7	17.5	12.1		20	69.1	
82.6	13.8	8.3		20	60.3	
82.8	24.6	22.3		20	90.9	
83.5	11.0	11.3		20	102.9	
83.8	12.2	12.4		20	101.4	
85.5	13.8	12.9		20	93.3	
85.8	12.1	11.5		20	94.4	

B.2.4 8 x Inlet Concentration

days after start up	% removal	removal (kg COD/m^3 bed.day)	average	flow rate (ml/min)	load (kg COD/m3 bed.day)	standard deviation for removal
86.6	59.2	12.1	12.8	20	126.1	6.47

90.1	10.7	10.9		20	102.5	
90.5	10.1	11.7		20	115.8	
90.8	11.6	13.4		20	115.4	
91.5	9.6	10.9		20	113.2	
91.8	12.1	13.6		20	112.0	
92.5	12.4	13.9		20	112.4	
92.9	13.9	15.5		20	111.2	
93.6	7.9	8.5		20	107.4	
103.0	14.5	18.2		20	125.2	
106.6	1.1	1.1		20	108.9	
106.9	18.4	20.1		20	109.3	
107.6	5.3	6.6		20	123.3	
110.1	9.9	11.1		20	112.6	
111.6	9.6	12.2		20	126.4	
111.9	1.2	1.5		20	123.5	
112.6	15.1	18.5		20	122.6	
112.9	15.5	18.8		20	121.8	
113.7	5.1	6.4		20	125.6	
117.0	15.9	20.4		20	128.2	
117.6	14.8	19.3		20	129.9	
117.9	3.7	4.8		20	129.4	
119.5	12.4	15.5		20	124.5	
119.8	5.6	6.9		20	123.5	
120.6	23.2	29.1		20	125.6	

B.2.5 16 x Inlet Concentration

days after start up	% removal	removal (kg COD/m^3 bed.day)	average	flow rate (ml/min)	load (kg COD/m3 bed.day)	standard deviation for removal
125.0	3.8	8.8	10.9	20	231.1	9.82

126.5	2.5	6.1		20	246.9	
126.8	6.8	15.8		20	232.4	
127.6	0.2	0.5		20	244.4	
130.1	4.8	12.2		20	252.3	
131.7	6.9	17.3		20	243.5	
131.9	2.0	4.7		20	237.1	
132.7	5.8	13.0		20	223.5	
132.8	2.4	5.9		20	248.1	
133.6	0.6	1.4		20	249.2	
137.0	10.7	28.0		20	261.0	
138.6	0.8	2.2		20	261.2	
139.0	4.9	12.5		20	256.3	
140.0	4.7	11.6		20	247.4	
140.6	1.6	4.2		20	260.7	
140.9	12.6	33.0		20	254.7	
141.6	0.4	1.0		20	252.5	
143.9	0.1	0.1		20	244.4	
144.7	0.6	1.5		20	258.1	
145.0	3.1	8.0		20	258.2	
145.6	1.3	3.3		20	258.1	
145.7	2.1	5.3		20	259.4	
145.8	7.5	19.2		20	254.9	
145.9	5.9	15.0		20	254.5	
146.0	0.4	1.0		20	253.8	
146.0	2.8	7.3		20	258.2	
146.1	0.5	1.3		20	253.7	
146.6	5.0	12.6		20	252.0	
147.1	3.5	8.9		20	254.4	
148.0	1.9	5.0		20	259.9	
148.5	3.7	9.7		20	259.3	
151.0	13.8	35.1		20	255.3	

151.6	8.1	21.1		20	259.5	
152.0	2.2	5.6		20	258.2	
152.7	1.3	3.2		20	253.5	
152.7	0.0	0.0		20	247.8	
152.7	11.0	27.7		20	248.2	
152.8	8.7	22.0		20	253.1	
152.8	11.5	28.4		20	247.8	
152.8	2.8	7.1		20	253.0	
152.8	3.5	9.0		20	256.3	
152.8	13.8	33.9		20	246.1	
152.9	9.9	24.8		20	251.2	
152.9	1.8	4.5		20	252.5	
152.9	10.6	26.6		20	250.6	
152.9	0.7	1.8		20	248.8	
153.0	1.1	2.7		20	253.0	
153.0	0.1	0.1		20	248.4	
153.1	0.8	2.0		20	247.5	
153.7	1.8	4.6		20	248.2	
154.0	1.6	3.9		20	247.0	
154.6	2.5	6.2		20	247.5	
155.0	3.8	9.8		20	255.9	
155.6	0.7	1.7		20	253.1	
159.1	9.6	22.1		20	230.6	
159.5	2.0	5.2		20	258.4	
160.0	8.7	22.7		20	260.7	
160.6	2.6	6.7		20	264.5	
161.0	4.2	10.8		20	256.2	
161.6	2.1	5.5		20	255.7	
162.1	11.7	28.5		20	244.4	
162.6	7.1	18.1		20	252.9	
164.9	9.2	24.2		20	262.6	

165.6	10.3	26.7		20	260.5	
166.1	9.5	23.8		20	250.7	

B.2.6 Removal Efficiency Curve Data

x times concentration	average loading (kg COD/m^3 bed.day)	average removal efficiency (%)	Standard Deviation for loading	Standard Deviation for removal efficiency
1	19.1	19.7	1.35	8.20
2	40.7	21.7	2.52	5.63
4	84.8	15.9	7.90	5.86
8	119.0	12.8	7.93	11.01
16	251.7	4.6	7.97	3.98

B.2.7 Removal Rate Curve Data

x times concentration	average loading (kg COD/m^3 bed.day)	average removal rate (%)	standard deviation for loading	standard deviation for removal rate
1	19.1	3.8	1.35	1.60
2	40.7	8.8	2.52	2.34
4	84.8	13.5	7.90	5.02
8	119.0	12.8	7.93	6.47
16	251.7	11.6	7.97	10.03

B.3 Gas Chromatography Result Data and Calculation

B.3.1 Condensate sample analysis result

Trial IV sample 1 Trial IV sample 2 Trial IV sample 3 Trial IV sample 4 Trial IV sample 5

tspan (s)	Average
1.130 - 1.150	733
1.210 - 1.250	3336
1.280 - 1.350	139
1.690 - 1.720	156
2.110 -2.160	269

tspan (s)	Average
<1.000	329
1.130 - 1.150	444
1.210 - 1.250	2538
2.110 -2.160	151

tspan (s)	Average
1.130 - 1.150	452
1.210 - 1.250	2869
2.110 -2.160	147

tspan (s)	Average
1.130 - 1.150	567
1.220 - 1.250	3549
2.000-2.100	325
2.110 -2.160	170

tspan (s)	Average
1.130 - 1.150	492
1.220 - 1.250	3208
2.110 -2.160	127

B.4 Data Comparing GC Analysis and COD Analysis on Filtration Result

B.4.1 Theoretical COD Calculation

reaction		methanol	+	oxygen	=	carbon dioxide	+	water
		CH3OH		O2		CO2		H2O
	1093.67	1		1.5		1		2
mmol/L		1.06		1.59		1.06		2.13
ppm		34.01		51.02		46.77		38.26

		ethanol	+	oxygen	=	carbon dioxide	+	water
		C2H5OH		O2		CO2		H2O
	2375	1		3		2		3
mmol/L		0.62		1.86		1.24		1.86
ppm		28.50		59.48		54.52		33.46

total oxygen needed: 110.50

B.4.2 Filtration using *MF-millipore membrane, mixed cellulose esters, Triton free, 0.45 μm, 25 mm* filter paper

date	time	Area count"in"		Area count "out"		Area count difference		COD			from calculation	% error
		meth	eth	meth	eth	meth	eth	in	out	difference		
25/11/2008	1100	17310	67154	15203	67402	2107	-248	2028	2002	26	110.50	324.99%
		16970	69308	16631	65511	339	3797					
		17457	68085	16622	64509	835	3576					
	average	17245.67	68182.33	16152.00	65807.33	1093.67	2375.00					
	1300	15651	70603	15343	68259	308	2344	2038	1996	42	47.89	14.03%
		15466	69299	15744	67816	-278	1483					
		15319	70272	15036	68945	283	1327					
	average	15478.67	70058.00	15374.33	68340.00	104.33	1718.00					
	1500	15419	70896	14644	64112	775	6784	2003	1852	151	299.70	98.47%
		16568	77443	16888	63417	-320	14026					
		15929	72035	13820	61720	2109	10315					
	average	15972.00	73458.00	15117.33	63083.00	854.67	10375.00					
	1700	15565	71051	15091	67563	474	3488	2000	1882	118	103.18	-12.56%
		17313	68855	15229	67807	2084	1048					
		15521	69885	15797	66312	-276	3573					
	average	16133.00	69930.33	15372.33	67227.33	760.67	2703.00					
	1900	15573	69440	15647	68264	-74	1176	1994	1986	8	-22.27	-378.36%
		15522	67886	15025	69604	497	-1718					

		15058	68312	15571	70270	-513	-1958					
	average	15384.33	68546.00	15414.33	69379.33	-30.00	-833.33					
	2100	15395	70893	17196	70159	-1801	734	2029	1972	57	211.20	270.52%
		17380	71814	13410	51480	3970	20334					
		17236	70742	17859	69390	-623	1352					
	average	16670.33	71149.67	16155.00	63676.33	515.33	7473.33					
	2300	17144	71625	17228	69773	-84	1852	1993	1983	10	122.82	1128.18%
		17090	70222	17151	68649	-61	1573					
		19590	71654	15842	67078	3748	4576					
	average	17941.33	71167.00	16740.33	68500.00	1201.00	2667.00					

B.4.3 Filtration using *MF-millipore membrane, mixed cellulose esters, Triton free, 0.22 μm, 25 mm* filter paper

date	time	Area count"in"		Area count "out"		Area count difference		COD			from calculation	% error
		meth	eth	meth	eth	meth	eth	in	out	difference		
11/12/2008	2200	1290	6050	1168	5683	122	367	133.5	125	8.5	20.39	139.84%
		1265	5887	1112	5587	153	300					
		1305	5923	1093	5055	212	868					
	average	1286.67	5953.33	1124.33	5441.67	162.33	511.67					
12/12/2008	1030	1218	5571	1109	5110	109	461	147.5	133.5	14	15.20	8.59%
		1208	5774	1143	5209	65	565					
		1239	5420			1239	5420					
	average	1221.67	5588.33	1126.00	5159.50	95.67	428.83					
18/12/2008	1030	1359	4693	826	2650	533	2043	172	141.5	30.5	58.99	93.41%
		1420	4986	859	2805	561	2181					
		1456	4649	1271	4189	185	460					
	average	1411.67	4776.00	985.33	3214.67	426.33	1561.33					
	1800	1309	6108	1115	6140	194	-32	168	155.5	12.5	16.11	28.86%
		1211	6832	1109	7129	102	-297					

				1065	5126	-1065	-5126					
	average	1260.00	6470.00	1096.33	6131.67	163.67	338.33					
19/12/2008	1030	774	3946	993	4734	-219	-788	168	145.5	22.5	3.80	-83.10%
		1062	5401	992	4422	70	979					
		1081	5110	1037	4650	44	460					
	average	972.33	4819.00	1007.33	4602.00	-35.00	217.00					
17/12/2008	2130	1113	8222	1117	6524	-4	1698	143.5	128	15.5	30.32	95.60%
		1124	8412	1080	6070	44	2342					
				1456	8171	-1456	-8171					
	average	1118.50	8317.00	1217.67	6921.67	-99.17	1395.33					
	1030	1097	4191	1081	3862	16	329	145.5	116	29.5	21.96	-25.56%
		1047	4154	1043	3695	4	459					
		970	4196	806	2696	164	1500					
	average	1038.00	4180.33	976.67	3417.67	61.33	762.67					
15/12/2008	2130	1109	4738	926	2219	183	2519	162	137.5	24.5	92.60	277.95%
		1303	6461	886	2323	417	4138					
		1315	5175	970	2500	345	2675					
	average	1242.33	5458.00	927.33	2347.33	315.00	3110.67					
14/12/2008	1800	966	4350	948	3798	18	552	154.5	131	23.5	16.68	-29.04%
		985	3813	942	3781	43	32					
		1127	4194	887	3341	240	853					
	average	1026.00	4119.00	925.67	3640.00	100.33	479.00					

B.4.4 Filtration using Centrifuge Filter

date	time	Area count"in"		Area count "out"		Area count difference		COD			from calculation	% error	% methanol	% ethanol
		meth	eth	meth	eth	meth	eth	in	out	difference			removal	removal
5/01/2009	2030	1254	5983	1122	5769	132	214	162	156	6	6.43	7.10%		
		1198	5791	1136	5684	62	107							
		1241	5640	1113	5791	128	-151							

	average	1231.00	5804.67	1123.67	5748.00	107.33	56.67						0.09	0.01
	2030	1294	5815	1194	5616	100	199	168	154	14	12.25	-12.49%		
		1258	5877	1203	5546	55	331							
		1289	5745	1193	5275	96	470							
	average	1280.33	5812.33	1196.67	5479.00	83.67	333.33						0.07	0.06
8/01/2009	930	1287	5341	891	4197	396	1144	160	119.5	40.5	48.94	20.83%		
		1213	5037	772	3229	441	1808							
				988	4326	-988	-4326							
	average	1250.00	5189.00	883.67	3917.33	366.33	1271.67						0.29	0.25
	930	1243	4979	1186	5144	57	-165	152	139	13	16.99	30.67%		
		1318	5418	1187	4709	131	709							
		1270	5090	1086	4292	184	798							
	average	1277.00	5162.33	1153.00	4715.00	124.00	447.33						0.10	0.09
9/01/2009	1000	1206	4651	673	2940	533	1711	168	114	54	60.32	11.71%		
		1126	4651	752	3149	374	1502							
		1217	4224	735	2798	482	1426							
	average	1183.00	4508.67	720.00	2962.33	463.00	1546.33						0.39	0.34
	1000	1191	4641	1142	4459	49	182	159	151	8	6.08	-24.06%		
		1165	4639	1112	4254	53	385							
		1133	4579	1168	4543	-35	36							
	average	1163.00	4619.67	1140.67	4418.67	22.33	201.00						0.02	0.04
13/01/2009	830	1398	6084	1212	5409	186	675	155	129	26	21.38	-17.75%		
		1240	6272	1249	5371	-9	901							
		1245	5932	1216	5330	29	602							
	average	1294.33	6096.00	1225.67	5370.00	68.67	726.00						0.05	0.12
	830	1309	5065	1251	4791	58	274	158	148	10	11.10	11.00%		

		1300	5092	1161	4992	139	100							
		1334	5434	1252	4998	82	436							
	average	1314.33	5197.00	1221.33	4927.00	93.00	270.00						0.07	0.05
14/01/2009	1030	1349	6029	1165	4768	184	1261	164.5	125	39.5	41.88	6.02%		
		1375	5862			1375	5862							
		1283	6476			1283	6476							
	average	1335.67	6122.33	1165.00	4768.00	170.67	1354.33						0.13	0.22
	1030	1421	5609	1145	5095	276	514	144.5	140	4.5	4.50	-0.04%		
		902	4223	1193	5107	-291	-884							
		1376	5597	1156	5070	220	527							
	average	1233.00	5143.00	1164.67	5090.67	68.33	52.33						0.06	0.01
15/01/2009	1000	1112	4747	1170	4692	-58	55	142	135	7	5.64	-19.41%		
		1202	4919	1075	4652	127	267							
						0	0							
	average	1157.00	4833.00	1122.50	4672.00	34.50	161.00						0.03	0.03
	1000	16844	72519	15416	69817	1428	2702	2032	1924	108	137.87	27.66%		
		16315	75597	15749	69746	566	5851							
		17169	73459	14775	73670	2394	-211							
	average	16776.00	73858.33	15313.33	71077.67	1462.67	2780.67						0.09	0.04
16/01/2009	830	941	2934	729	2656	212	278	137.5	116.5	21	21.84	4.01%		
		881	2983	661	2034	220	949							
		895	2970	718	2715	177	255							
	average	905.67	2962.33	702.67	2468.33	203.00	494.00						0.22	0.17
	830	16709	76612	14057	69984	2652	6628	1993	1843	150	189.62	26.41%		
		15730	72076	15118	69641	612	2435							
						0	0							

	average	16219.50	74344.00	14587.50	69812.50	1632.00	4531.50						0.10	0.06
19/01/2009	1030	1170	5963	1024	5024	146	939	162.5	140	22.5	26.86	19.39%		
		1119	5724	1009	5268	110	456							
		1142	5982	1135	4649	7	1333							
	average	1143.67	5889.67	1056.00	4980.33	87.67	909.33						0.08	0.15
	1030	14649	75722	14823	69155	-174	6567	1980	1892	88	115.26	30.98%		
		14712	76594	15158	69427	-446	7167							
		14894	70699			14894	70699							
	average	14751.67	74338.33	14990.50	69291.00	-238.83	5047.33						-0.02	0.07
20/01/2009	1100	1100	5549	1031	4924	69	625	156.5	146.5	10	12.67	26.69%		
		1119	5405	1121	4795	-2	610							
		1107	5016	1055	4955	52	61							
	average	1108.67	5323.33	1069.00	4891.33	39.67	432.00						0.04	0.08
	1100	14464	70314	14325	67111	139	3203	1974	1911	63	79.48	26.16%		
		15656	67206	14373	68597	1283	-1391							
		14984	71174	14631	66771	353	4403							
	average	15034.67	69564.67	14443.00	67493.00	591.67	2071.67						0.04	0.03
27/01/2009	930	834	3412	836	3147	-2	265	157	141.5	15.5	13.00	-16.11%		
		957	3925	861	3545	96	380							
		995	3782	853	3309	142	473							
	average	928.67	3706.33	850.00	3333.67	78.67	372.67						0.08	0.10
	930	10371	40278	9617	37408	754	2870	2000	1899	101	109.61	8.52%		
		10965	40963	9300	36065	1665	4898							
		9659	37219			9659	37219							
	average	10331.67	39486.67	9458.50	36736.50	873.17	2750.17						0.08	0.07
28/01/2009	1000	873	3514	889	3240	-16	274	132	112.5	19.5	22.32	14.48%		

		791	3110	679	2332	112	778							
		893	3649	736	2498	157	1151							
	average	852.33	3424.33	768.00	2690.00	84.33	734.33						0.10	0.21
	1000	11124	45322	11594	51271	-470	-5949	1997	1877	120	124.56	3.80%		
		11592	45702	10551	42516	1041	3186							
		11383	46860	8887	34889	2496	11971							
	average	11366.33	45961.33	10344.00	42892.00	1022.33	3069.33						0.09	0.07
29/01/2009	1030	605	1893	310	951	295	942	118.5	99	19.5	14.16	-27.38%		
		641	2174	559	1749	82	425							
		507	1767	602	1963	-95	-196							
	average	584.33	1944.67	490.33	1554.33	94.00	390.33						0.16	0.20
	1030	11885	50832	11458	45750	427	5082	1953	1870	83	139.21	67.72%		
		11385	49493	11760	49967	-375	-474							
		12579	54976	11836	44389	743	10587							
	average	11949.67	51767.00	11684.67	46702.00	265.00	5065.00						0.02	0.10
30/01/2009	1030	724	2458	695	2305	29	153	166.5	141.5	25	26.69	6.77%		
		1081	3840	657	2447	424	1393							
		823	2910			823	2910							
	average	876.00	3069.33	676.00	2376.00	200.00	693.33						0.23	0.23
	1030	13137	52273	11325	43679	1812	8594	1972	1843	129	127.60	-1.09%		
		12196	49253	12375	47570	-179	1683							
		12509	44611	11558	44416	951	195							
	average	12614.00	48712.33	11752.67	45221.67	861.33	3490.67						0.07	0.07
2/02/2009	830	693	2973	526	1892	167	1081	122	93.5	28.5	37.69	32.23%		
		777	2830	402	2117	375	713							
		872	2938	522	1879	350	1059							

	average	780.67	2913.67	483.33	1962.67	297.33	951.00						0.38	0.33
	830	12775	51271	12404	51268	371	3	1846	1759	87	82.93	-4.68%		
		13187	58297	12231	51806	956	6491							
		11857	45101	11239	45284	618	-183							
	average	12606.33	51556.33	11958.00	49452.67	648.33	2103.67						0.05	0.04
												Average	0.111	0.116